CHEMICAL PROBLEMS IN HIGH-PRESSURE BOILER OPERATION.

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PREFACE.

In the 35 years since the differential aeration theory gave an explanation of the role of oxygen as a corrosion factor (1), extensive work has been carried out on the estimation of dissolved oxygen in boiler feed - water.

The increased use, in recent years, of high pressures and temperatures with the associated high ratings of boiler heat - transfer surfaces, has increased the dangers arising from corrosion attributed to dissolved oxygen. This then seemed an apt time to review the problems involved in the estimation of oxygen dissolved in boiler feed - water and in particular the effect reducing agents present in this water have on the estimations.

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CHAPTER 1.

CHEMICAL METHODS BASED ON THE WINKLER REACTIONS.

1: 1. THE WINKLER REACTIONS.

The majority of the chemical techniques at present used to estimate oxygen dissolved in boiler feed - water are either modifications of the classical Winkler method (2) or are based on a similar reaction procedure. Winkler's method was devised to determine the oxygen content of natural waters and it is quite satisfactory for this purpose unless a high degree of accuracy is required. However there are certain inherent errors which make the original method unsuitable for boiler feed - water analysis. Winkler made use of the fact that a suspension of manganous hydroxide is rapidly oxidised by dissolved oxygen to a mangano - manganic hydroxide which, in acid solution, reacts with potassium iodide to release iodine. The latter was estimated by sodium thiosulphate with starch as an indicator.

The Winkler reactions may be expressed as:-

(a) $2\,Mn(11) + 4OH^- \rightarrow 2\,Mn\,(OH)_2$

(b) $2Mn(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2\,Mn\,(OH)_3$

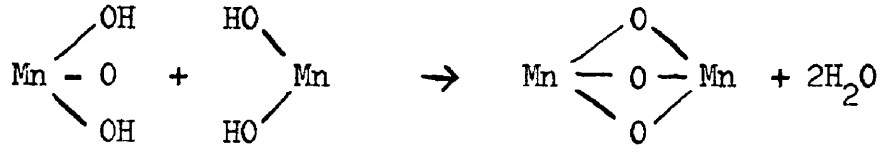
(c) $2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow 2\,Mn\,(11) + I_2 + 6H_2O$.

The iodine released is therefore equivalent to the dissolved oxygen originally present in the solution, and the actual oxidised form of the manganese does not affect the amount of iodine liberated. Freier (3) gives the manganese reactions as:-

(d) $Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow Mn\,O\,(OH)_2$

and

(e)



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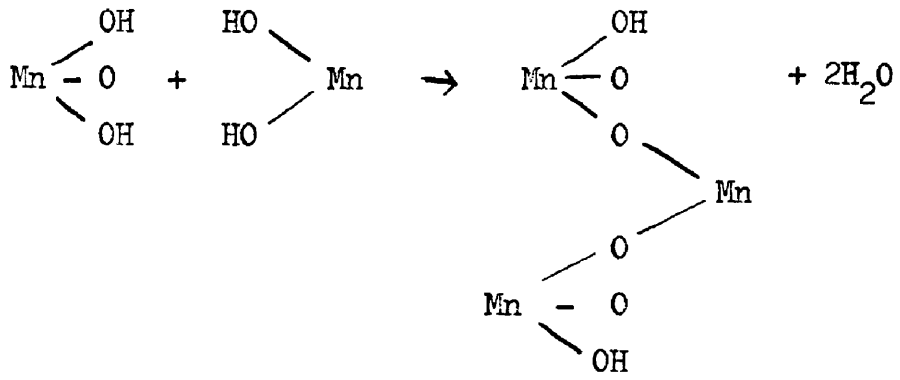


1:2. SOURCES OF ERROR IN THE WINKLER METHOD.

The development of accurate estimations of dissolved oxygen in boiler feed - water has been dependent on techniques designed to overcome the errors in the Winkler method. There are three main sources of error;

(i) dissolved oxygen introduced by the reagents,

(ii) the starch/iodine blue complex does not appear until an appreciable concentration of iodine is present,

(iii) no allowance is made for oxidising or reducing agents present in the test water.

Knowles and Lowden (4) found that iodine equivalent to 0·028 and 0.016 p.p.m. of dissolved oxygen had to be added to 50 ml. and 200 ml. of water respectively before the blue starch colouration was observed. Bairstow (5) gives the value as 0·014 p.p.m. for a 250 ml. sample and Potter (6) holds that the threshold value is equivalent to 0·017 p.p.m. of dissolved oxygen. Although there appears to be a lack of unanimity regarding the exact value of this error it would appear to be in the region of 0·010 - 0·020 p.p.m. of dissolved oxygen.

The second source of error in the classical Winkler method is the dissolved oxygen contained in the reagents. A study of equations (a) and (b) shows that any dissolved oxygen in the alkaline or manganous reagents will also react so as to release an equivalent amount of iodine. This leads to a result greater than the true value. It is difficult to obtain a generally recognised figure for the dissolved oxygen in the reagents due to the variation in both the concentrations and the volumes of reagents used. The A.S.T.M. method (7) requires a 500 ml. sample and 2 ml. of each reagent and gives a correction of 0.010 p.p.m. This correction was obtained from tests performed by Adams (8). However in the discussion following this paper it was stated that other figures corresponding to a correction of 0·020 p.p.m. had been obtained by previous workers (9). Wickert (10) and Bairstow (5) using different quantities of different reagents and smaller samples give a correction of 0·024 p.p.m. and 0·007 p.p.m. respectively.

The above data shows that when dissolved oxygen values below 0·100 p.p.m. are determined, consideration must be given to the oxygen contained in the reagents. Compensation for this error is discussed in section 1:4.

The most serious problem encountered when the Winkler method was developed for boiler feed - water analysis was the interference caused by reducing agents.

These reducing agents in the boiler water can be either the chemicals such as hydrazine or sodium sulphite introduced as oxygen scavengers or the ferrous and cuprous ionsproduced as a result of tube corrosion. These substances become very active reducing agents in alkaline solution and it follows from equations (a), (b), and (c), that reducing agents will result in a decrease in the final iodine concentration and low estimations of the dissolved oxygen content. The magnitude of this interference naturally varies and it is now held that the classical Winkler reaction is useless below 0·06 p.p.m. when reducing agents are present.

1:3. DEVELOPMENT OF THE A.S.T.M. "REFEREE" METHOD.

It has been by a gradual realisation of the magnitude of the errors discussed in Section 1:2 that it has been possible to devise methods of reducing the combined error and to estimate dissolved oxygen in boiler feed - water with any degree of accuracy.

Schwartz and Gurney (11) devised a method which compensates for the effect of reducing agents. They introduced the "reversed - reagents" technique in which two simultaneous samples are collected, one of which serves as a blank. The order of reagent addition was:-

Sample	(i)	alkaline iodide solution
	(ii)	manganous solution
	(iii)	acid.
Blank	(i)	alkaline iodide solution
	(ii)	acid
	(iii)	manganous solution.

The equations of the Winkler reactions show that;

iodine produced in the sample. = dissolved oxygen - (effect of reducing agents + effect of reagent impurities).

and iodine produced in the blank. = effect of reducing agents + effect of reagent impurities.

This is because no manganous hydroxide is formed in the blank and the dissolved oxygen reactions are therefore eliminated. Therefore a measure of the dissolved oxygen alone should be obtained when the two iodine titrations are subtracted. This double titration is one possible method of reducing the error arising from the use of starch as an end - point indicator. If the concentration of iodine needed to develop the blue clour is constant then the error would be expected to cancel when the two iodine titrations are subtracted.

It is quite possible to obtain a blank or even a sample that produces no blue colour with starch after the reagent additions. This depends on the relative concentrations of reducing agents and oxygen. Schwartz and Gurney in this case added a known amount of the oxidising agent potassium bi-iodate to produce a blue colour and then titrated.

Several refinements have been made to the "reversed-reagents" method, and it is now common practice to add an oxidising agent with the alkaline iodide solution. The order of the "reversed - reagent" addition is important as, wherever possible, the same pH conditions should prevail in the sample and blank. This is of particular importance when reducing agents are present since these usually react faster in alkaline solution.

In power stations many chemists using the sample and blank technique do so incorrectly. Often the order of reagent addition is:-

Sample	(i)	alkaline iodide/iodine
	(ii)	manganous sulphate
	(iii)	sulphuric acid.
Blank	(i)	sulphuric acid
	(ii)	manganous sulphate
	(iii)	alkaline iodide/iodine.

The use of this order of reagent addition can introduce errors if reducing agents are present as the oxidation of the interference does not take place in alkaline solutions in both cases. Hence conditions in the sample favour a more complete oxidation of the reducing impurities normally associated with boiler feed - water than is achieved in the blank and consequently a greater diminution of the concentration of the added oxidising agent occurs in the sample. This defeats the purpose of the reversed - reagents technique and shows that the only satisfactory order is:-

Sample	(i)	alkaline iodide/iodine
	(ii)	manganous sulphate
	(iii)	sulphuric acid.
Blank	(i)	alkaline iodide/iodine
	(ii)	sulphuric acid.
	(iii)	manganous sulphate.

In 1943 Adams and colleagues (8) published results of an investigation on the "reversed - reagents" method. It was shown that about ten sample volumes should flow through the sampling vessel before the water in the vessel can be adjudged a true sample. An important innovation claimed for this work was the introduction of free

iodine into the alkaline iodide solution and this has generally replaced the use of potassium bi-iodate as an oxidising agent. They added the reagents in the order which was shown, in the previous paragraph, to be satisfactory.

This order of reagent addition has been adopted by the A.S.T.M. in their standard procedure (7).

Ulmer and co-workers (12) adopted the same reaction scheme as Adams but overcame the effect of interference in a different manner. They took a 500 ml.sample and two 250 ml. samples. They then added the Winkler reagents to the 500 ml. sample and to one of the 250 ml. flasks. The 500 ml. of solution was titrated with thiosulphate then the 250 ml. of treated sample was mixed with the other 250 ml. of sample water and the resulting solution was also titrated. They assumed that:-

iodine produced in 500 ml. of fixed solution	=	oxygen in 500 ml. water + oxygen in reagents - interference in 500 ml.
and iodine produced in 250 ml. fixed solution + 250 ml. water	=	oxygen in 250 ml. water + oxygen in reagents - interference in 500 ml.,

and that subtraction of the two titres would give the dissolved oxygen contained in 250 ml. of the water under test. Unlike Adams, they did not add a free oxidising agent but if a reducing reaction was given after the fixing process a known amount of potassium iodate was added before the titration.

The assumption that in both cases a factor is included for the interference found in 500 ml. can be criticised as in one case 250 ml. of the water is never alkaline. The reason for the criticism is similar to that put forward against a completely reversed blank earlier in this section.

Sebald (13) compared the methods of Winkler, Schwartz and Gurney, and Adams. The results obtained when impurities were present pointed to the method of Adams being preferable to the others.

The synthesis of the work of the authors mentioned in this section forms the A.S.T.M. standard for the estimation of dissolved oxygen (7).

1:4 COMPENSATION FOR THE EFFECT OF OXYGEN DISSOLVED IN THE REAGENTS.

The magnitude of the error introduced by the oxygen dissolved in the reagents has been shown to be as much as 0·010 p.p.m. Winkler (2) used concentrated reagent solutions and thus depressed the solubility of the non-electrolyte, oxygen. The equations of the Winkler reaction show that it requires 10g. of manganous sulphate

to reduce 1 g. of oxygen providing no equilibria are set up. The A.S.T.M. test (7) requires the addition of 1 g. of manganous sulphate to measure 0·001 - 0·100 mg. of oxygen. It is obviously possible to reduce the volume of the reagent additions and hence minimise the introduction of oxygen with the reagents.

Yoder and Dresher (9) in 1933 recognised the effect of oxygen dissolved in the reagents and corrected for it. They continued to use 2 ml. volumes of reagents and this trend appears to be common in British and American work. The German workers, Zimmerman (14), Wickert (10), and Schumann (15), used smaller reagent volumes before this became fashionable in Britain.

The triple - sample technique is one method of compensation and was described in section 1:3. The oxygen in the reagents was sometimes estimated by performing the "reversed - reagents" technique in duplicate (11). Double the volume of reagents was added to one set of samples than was added to the other. The difference in the dissolved oxygen values obtained in the two sets is the dissolved oxygen added with the smaller volume of reagents. Hence by subtraction the true oxygen value of the water may be obtained. The main criticism of this must be on account of its complexity.

The usual method is to apply the A.S.T.M. correction of 0·010 p.p.m., without correction for the prevailing temperature and pressure. This, and the fact that the correction is often greater than the oxygen being estimated, makes it more satisfactory to render the reagents "oxygen - free". This is the method adopted in the present work.

One possible method of deaerating the reagents below the detectable limit would be to boil the reagents just before use. However this is not practical due to the possibility of decomposition. Other methods are similar to those detailed in Section 7:1.

1:5. END - POINT DETERMINATIONS.

A certain concentration of free iodine must be present before any colouration is discernible when starch is added. It has been noted in section 1:3 that the error introduced by this "threshold" value was reduced by the "reversed - reagents" technique. Freier (16), in 1954, used starch as an indicator but it is probably significant that in 1955 he changed to a potentiometric end - point determination (17).

Accurate estimations of dissolved oxygen are now almost exclusively carried

out using an electrometric determination of the iodine/thiosulphate titration end - point. Adams (8) used a normal potentiometric titration with calomel and platinum electrodes. Hewson and Rees (18) and others (12) developed a "dead stop" end - point titration incorporating two bright platinum electrodes.

Variations on these two methods have been made in recent years. Knowles and Lowden (4 & 19) developed the simple amperometric circuit shown in fig.1a which gives a titration curve of the form shown in fig. 1d. Knowles and Lowden considered that a back titration produced more satisfactory results. Their results show that the method can detect iodine equivalent to 0·001 - 0·0015 p.p.m. of oxygen. These were the concentrations in which they were interested but their graphs show that the end - point can be estimated to an iodine concentration equivalent to approximately 0·0003 p.p.m. of oxygen. Unfortunately neither of the publications on this method states the accuracy obtained in dissolved oxygen determinations using this technique. One important advantage inherent in this technique is that impurities do not interfere with the end point as they only contribute to the residual current (horizontal part of curve) and the end - point is still determined by a positive increase in the current.

The amperometric technique has been developed by Young (20 and 21) by the incorporation of a resistance and the measurement of the varying potential drop across the resistance with a pH meter (fig.1b). Young found that a rotating platinum electrode gave a more satisfactory response both in respect of obtaining steady conditions after a titrant addition and the magnitude of the diffusion current (22). Young claimed that this circuit enabled determinations to be made with a precision of 0·0001 p.p.m. (21). Potter and co-workers developed another modification (6) which responded to an iodine concentration equivalent to 0·00004 p.p.m of oxygen.

The work of Potter and Young will be referred to frequently but it is sufficient to note at present that the iodine produced in the Winkler reactions can be estimated to a dilution below that at present applicable to oxygen estimations. Potter discusses the relative merits of the potentiometric and amperometric end - point determinations and concludes that whereas the potentiometric method may suffer interference from other redox systems present in the solutions, e.g. metal ions, which may limit it to a precision of 0·001 p.p.m. in an oxygen analysis, the

amperometric methods can be refined to give increased sensitivity. He favoured measuring the potential drop across an external resistance with a pH meter rather than using the simple circuit incorporating a galvanometer only, as it was difficult to achieve stability with a high sensitivity galvanometer. Bargh (28), however, found difficulties in the response of the platinum/tungsten electrode system and returned to the "dead-stop" potentiometric estimation of the end - point.

Various methods have been proposed in which the end - point is estimated by colorimetric means. Bairstow (5) measured the starch/iodine/iodide blue complex with a "Spekker" photoelectric absorptiometer but found that each new stock of starch required recalibration and temperature control was essential if an accuracy of 0·003 p.p.m. was to be attained. Ovenston and Watson (23) added a higher concentration of iodide ion producing tri-iodide ion which was estimated by a spectrophotometer. Slight variations in temperature had little effect on the results and a precision of about 0·001 p.p.m. was claimed.

Banks (24) added sodium acetate buffer then 3:3' - dimethylnaphthidene to the iodine produced in the Winkler reactions and measured the resulting colour with a photo-electric colorimeter. As he did not have a supply of water containing oxygen in the range 0 - 0·015 p.p.m., the results in this range were obtained by diluting the iodine produced by the Winkler reactions in higher ranges. An accuracy of $\pm$ 0·003 p.p.m. was claimed for this method.

Zimmerman (14) attempted to improve the sensitivity of the o - tolidine method by drawing off the supernatant liquid from the manganese hydroxide precipitate, acidifying the precipitate with phosphoric acid, then making up to 40 ml. with distilled water and estimating the yellow colour photometrically. This method was refined by Wickert (10) who displaced the supernatant liquid with carbon dioxide to prevent oxygen contamination. This technique is designed to concentrate the effect of the oxygen and can obviously only be used on the sample as in the blank no precipitate is obtained. It is therefore of doubtful accuracy to attempt to increase the sensitivity of the sample without duplicating this sensitivity in the blank particularly at low oxygen levels when the value of the sample approaches that of the blank, in addition the risk of displacing some precipitate or introducing oxygen is considerable.

Another attempt to increase the sensitivity was by extracting the iodine

produced in the Winkler reactions with carbon tetrachloride (25 and 26). The procedure appears somewhat tedious as it involves extracting with carbon tetrachloride, adding water to the extract, running in an excess of standard thiosulphate, and back titrating with iodine. Moreover the amount of solvent used for an 1100 ml. sample seemed to vary from the normal of 120 ml. to 160 ml. or more. The method suffers from the disadvantage that I_3^- ion is present which is more soluble in water than I_2 therefore does not extract completely in the solvent layer. It is unlikely that this method or the alternate form of estimating the colour produced in the solvent layer directly offers advantages over the electrical methods of end - point determination.

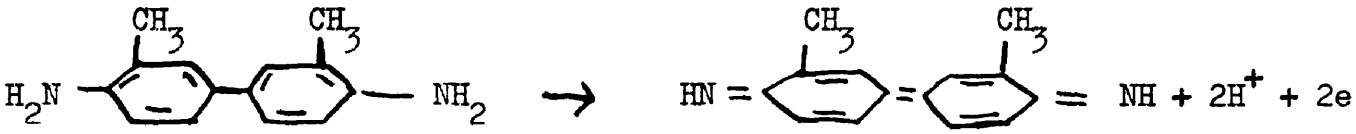
It can be said that in general the colorimetric estimations have no advantages over the electrometric determinations of the end - point as, in most cases, the purity of reagents, regulation of temperature, colour development time, and contamination from the atmosphere are all critical factors. Most of the methods quoted in which the coloured solution is concentrated before being estimated could have obtained the desired result, more simply, by using a long - cell absorptiometer.

CHAPTER 2.

METHODS BASED ON MODIFICATIONS OF THE WINKLER REACTION SCHEME.

2:1. THE INTRODUCTION OF O-TOLIDINE.

In 1929 McCrumb and Kenny introduced o-tolidine as a reagent for the determination of dissolved oxygen (27) as there is a marked colour change associated with the oxidation of this compound.



Reduced form (colourless) "A"

Oxidised form (yellow) "B"

The reaction scheme used o-tolidine instead of iodide and reactions were:-

(a) $2Mn(11) + 4OH^- \rightarrow 2\ Mn(OH)_2$

(b) $2Mn(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2\ Mn(OH)_3$

(c) $2Mn(OH)_3 + \text{"A"} + H^+ \rightarrow 2\ Mn(11) + \text{"B"} + H_2O.$

McCrumb and Kenny found that at low oxygen values the colour developed was not proportional to the oxygen concentration. They attributed this to an equilibrium reaction and found an o-tolidine concentration of 10 g./lr. gave satisfactory results. Haslam and Moses (29) reinvestigated the method and found that many of the earlier difficulties could be overcome by purification of the reagents. They also refined the preparation of the permanent colour standards which were obtained by mixing differing amounts of potassium dichromate and copper sulphate solutions. These are useful in boiler - house laboratories as a speedy method of estimating the o-tolidine colour as an oxygen equivalent but cannot be applied to accurate work. Haslam and Moses give $\pm$ 0.005 p.p.m., in the range 0·002 - 0·050 p.p.m. of dissolved oxygen, as the accuracy of the method.

McCrumb and Kenny did not include iodide in their reagents and attributed their difficulty in dissolution of manganese hydroxide to the absence of hydriodic acid. However, they used small sample volumes and if the ordinary Winkler technique

is performed with small test volumes similar difficulties arise and usually a slight precipitate of a chocolate - brown colour remains undissolved. This was found in the present work but was overcome simply by the use of smaller volumes of reagents since the normal reagent volumes are considerably in excess of the actual amount required.

It has been standard practice to use chlorides in this reaction, but a study of the oxidation potentials shows that the reaction can proceed without having free chlorine as an intermediate oxidising agent. The reaction would then be:-

$$Mn^{+++} + \underset{\text{(colourless)}}{\text{o-tolidine (reduced form)}} \rightarrow Mn^{++} + \underset{\text{(yellow)}}{\text{o-tolidine (oxidised)}}$$

Freier (3) gives the E_o values for Mn^{+++} and o-tolidine as 1·49 and 0·87 volts respectively. Thus it can be seen that the reaction between these two substances should proceed as shown without free chlorine being present.

2:2. THE USE OF CERIUM.

Schumann (15) has recently developed a modification of the o-tolidine method in which manganese salts are replaced by cerium salts. The reactions and techniques are similar to the original method. The change is stated to improve the estimation as cerium has only two oxidation states with an E_o potential of + 1·6 compared with that of manganese of + 1·5 enabling the theoretical degree of completeness of reaction with oxygen to be higher. Two other factors are that cerium (III) salts are colourless and the cerium (IV) salts are yellow, also the cerium hydroxide precipitate settles leaving the supernatant liquid clear. The latter point is important as Zimmerman (14) obtained a more concentrated colour by siphoning off the supernatant liquid under an inert atmosphere before acidifying the hydroxide precipitate. It was also claimed that the reaction between Ce(IV) and o-tolidine gives the same pure colour whilst the use of manganese salts results in a slight variation of colour from experiment to experiment.

Schumann also states that ceric salts will oxidise the reducing agents, present in boiler feed-water, in acid solution thus counteracting the errors produced by reducing ions. This effect would not enable accurate results to be obtained by the method he used, as this consisted of treating a single sample and using reagents containing no free oxidising agents.

i.e. $Ce(III) + (O) + e \rightarrow Ce\ (IV) + O^{=}$

and $Ce\ (IV)$ + o-tolidine $\rightarrow Ce(III)$ + o-tolidine (yellow)

If reducing agents were present the reaction would become:-

$$Ce(III) + (O) + e \rightarrow Ce(IV) + O^{=}$$

$$Ce(IV) + \left\{\begin{array}{l}\text{reducing agent}\\ \text{o-tolidine}\end{array}\right. \rightarrow Ce(III) + \left\{\begin{array}{l}\text{Oxidised form of}\\ \text{reducing agent}\\ +\\ \text{o-tolidine (yellow)}\end{array}\right.$$

and the final yellow colour would not truly represent the dissolved oxygen originally present, as it would contain an error proportional to the reducing agent concentration.

The use of cerium salts, therefore, does not render the "reversed - reagents" technique unnecessary, and free oxidising agents must still be added as ceric ions must be present before any yellow colour is produced and in the blank, as dissolved oxygen does not react, no ceric ions would be produced, hence no diminution of colour intensity, which is the purpose of the blank, could be obtained.

CHAPTER 3.

DIRECT CHEMICAL METHODS.

3:1. THE INDIGO-CARMINE METHOD.

Estimations of dissolved oxygen by a direct method is attractive as it means fewer reagents and hence simpler operative technique. The majority of the proposed direct methods rely on the oxidation of a colourless solution by dissolved oxygen to a coloured solution and the latter is measured by photometric means.

Efimoff (30) used indigo-carmine as a colorimetric reagent to determine dissolved oxygen in connection with biological studies. An accuracy of 0·5 - 1 p.p.m. was considered satisfactory in this work. Buchoff, Ingber, and Brady (31) developed the indigo-carmine method to make it applicable to boiler feed-water studies. They employed a leuco reagent solution of indigo-carmine which, on addition to the water under test, gave a range of colours according to the dissolved oxygen present.

p.p.m. O_2	colour
0·005	greenish-yellow
0·015	orange
0·028	red
0·062	reddish-purple

The method appeared to compare favourably with the A.S.T.M. method (7) when both were performed simultaneously. Sulphite ions had little effect on the method but interference was encountered when ferrous ions were present. The apparatus consisted of a cylindrical sampling tube containing a small phial of reagent attached to the inside wall, the mouth of the latter being closed by a glass ball. When the sample had been collected the tube was inverted, the ball-seal fell out, and reagent mixed with the test sample. The operations are therefore very simple. The problem of interference from ferrous ions was assumed to be capable of solution by incorporation of a anion resin column. However, complications would arise due to the regeneration of the beds by air - saturated water. This will be discussed in Chapter 4.

The major fault with the majority of the direct methods is that the oxidised reagent is usually of a quinonoid-type structure. This structure is usually susceptible to reduction which is the explanation for the majority of these methods

failing in the presence of reducing agents. Another factor that must be considered is that a quinonoid form may form a complex with metal ions thus altering the colour intesity and hence making it impossible to obtain correct results when a calibration from pure water is used. In these connections it is interesting to note that Buchoff and co-workers state that no interference was found from nickel, cupric, or zinc ions. These,if they interfered, would only do so by forming complexes. The fact that the ferrous ions interfere shows that the reagent is susceptible to a reducing or a complexing action, although the fact that sulphite did not appear to interfere may indicate that it was the latter effect. It is possible that a similar interference would be shown by cuprous ions which was not investigated.

The Russian workers in the field of dissolved-oxygen analysis have made strong claims on the efficacy of the indigo-carmine method. The following notes give the experiences as recorded in the literature.

(a) Buchoff et al. (31).

They found that Ni, Cu^{++}, or Zn (1 p.p.m. of each) gave no interference. Neither did Fe^{+++} (3 p.p.m.) or SO_3^{--} (0.012 p.p.m.).

Fe^{++} interfered in all concentrations.

Oxygen range claimed = 0- 0.050 p.p.m.

Precision claimed = 0.002 p.p.m.

(b) Babkin (104).

NO_2^-, NO_3^-, SO_4^{--}, Cl^-, Zn, Fe^{++}, or Fe^{+++}, gave no interference.

SO_3^{--} (above 12 p.p.m.) or Cu^+ gave interference.

(c) Wickert (105).

Fe^{+++} (2 p.p.m.) or SO_3^{--} (1.5 p.p.m.) gave no interference.

Interference was found with $S_2O_4^{--}$,(0.010 p.p.m.), Fe^{++}(any concentration or with hydrazine above 0.5 p.p.m.

The lower level of oxygen analysis was 0.003 p.p.m. and the accuracy was 0.002p.p.m. - 0.003 p.p.m.

(d) Babkin (106).

$SO_3^{--}$and NO_2^- gave no interference whilst Cu^+ or Fe^{++} did.

(e) Alcock and Coates (87) did not test the method with reference to specific interferences.

The concentrations in (a)- (e) above refer to individual impurity concentrations.

It would appear from the literature quoted that the indigo-carmine method has been tested at the oxygen levels required for normal feed-water analysis. The interferences, being mainly ionic, could be removed by ion-exchange resins if precautions were taken (Chapter 4). Some of the authors quoted have used complexing agents to eliminate specific interferences.

Babkin (107) makes the interesting claim that indigo-carmine is not subject to the "uncorrected-interference" arising from oxidation of a reducing agent by the oxidised manganese which is produced in the "sample" of a "reversed-reagents" oxygen analysis (see Chapter 12).

The indigo-carmine method, as stated earlier, has been widely accepted in the U.S.S.R. as the routine method of oxygen analysis. It remains to be seen if the method is capable of being refined to the precision attained by Potter (6) for the A.S.T.M. method.

3:2. ESTIMATION BY DIRECT TITRATION.

A direct titration method has been reported by Hungarian workers (32) in which the dissolved oxygen oxidised ferrous ammonium sulphate in alkaline solution. The ferric ion was then titrated, after acidification, by a 0.01 $\overline{N}$ ascorbic acid solution with 4 - amino 4' methoxydiphenylamine as an indicator. From the data shown which were for air-saturated water, the agreement with the Winkler method was very satisfactory. Nitrite ions did not appear to interfere. Details of the ascorbic acid/ ferric ion reaction were published in 1952 (33).

The use of ferrous ions may have some advantage over manganous ions as Todt (34) found that ferrous hydroxide was oxidised faster than manganous hydroxide by dissolved oxygen.

In 1954 Stone and Sigal (35) published a titrimetric method of oxygen estimation in the presence of nitrites using chromous solutions. The basis of the method was to add a known excess of chromous reagent to the sample, followed by a known excess of iodate solution and back titrating with chromous reagent after adding iodide crystals. Starch was used as an indicator.

In the presence of nitrites acidified potassium permanganate was added in excess and after 5 minutes oxalic acid was added to remove the excess permanganate. This procedure took up to 20 minutes. The water was air-saturated and a satisfactory agreement was achieved when compared with both the Winkler method and the theoretical values. It is unlikely that these methods would be used for boiler feed-waters as the complexity is greater than the A.S.T.M. method when reducing agents are present.

CHAPTER 4.

INTERFERENCE.

The oxidising or reducing reactions of various impurities present in natural waters and boiler feed - water has proved to be a major factor in preventing accurate results being obtained in dissolved oxygen determinations. Among the most frequently encountered impurities are nitrite, sulphite, ferrous, and cuprous ions, and also hydrazine.

Various authors have reported reagents used to oxidise specific interferences, Alsterberg (36) added sodium azide to oxidise nitrite. Rideal and Stewart (37) used acid permanganate for this purpose but Theriault and McNamee (38) reported that this reagent set up an equilibrium with sulphite ion and therefore failed to oxidise the sulphite interference completely. The latter authors found that hypochlorite in alkaline solution provided a satisfactory oxidant for sulphite.

It would be impracticable to attempt to determine dissolved oxygen by adding the various reagents given in the literature as having been found to be the most suitable for specific impurities. It is obvious that it is desirable to use as an oxidiser one substance that is capable of oxidising all the impurities present in boiler feed - water. This has been resolved in recent years to the use of alkaline/ iodine (7), potassium iodate (6), bromine water (39), or alkaline permanganate (22).

The use of the sample and blank technique has proved to be the most effective way of overcoming errors due to interfering substances. However, in recent years attention has been redirected to this problem. Originally it was assumed that in the sample and blank technique (taking "R" as the reduced form of the interference and the A.S.T.M. method) the reactions were:-

SAMPLE.

				pH of Solution.
(i)	$2R + I_2$	$\rightarrow$	$2R^+ + 2I^-$	usually alkaline.
(ii)	$Mn(II) + (O)$	$\rightarrow$	$Mn(III)$	alkaline.
(iii)	$Mn(III) + 2I^-$	$\rightarrow$	$Mn(II) + I_2$.	acid.

BLANK.

(IV)	$2R + I_2$	$\rightarrow$	$2R^+ + 2I^-$	usually alkaline.

It appears to have been originally assumed that reactions (i) and (IV)

completely eliminated the interference. This would be so only when there was an irreversible reaction or one which, to all practical purposes, was irreversible. This would be the case with a few of the more common impurities, e.g. hydrazine can be oxidised to nitrogen under certain conditions, which would render the reaction irreversible, however, reactions e.g. those which depend only on electron transfer can possibly give a reversible reaction when the hydroxide precipitate is acidified. The extent to which this reaction proceeds is of course dependent on (a) the oxidation - reduction potential of both the interfering ion and that of the substance to be oxidised - iodide, o-tolidine, indigo - carmine etc., and (b) the relative concentrations of the various ion species present. This is particularly so with the metallic cations, such as iron, which would give the following reaction sequence:-

$$Fe(II) + \text{oxidiser} \rightarrow Fe(III)$$

$$Fe(III) + 3\,OH^- \rightarrow Fe(OH)_3$$

$$\text{or} \quad Fe(II) + 2OH^- \rightarrow Fe(OH)_2 \xrightarrow{\text{oxidised}} Fe(OH)_3$$

It must have been held, however, that, as this would logically occur to the same extent in the sample and the blank, that when the solution was acidified the result would be

$$2\,Fe(III) + 2I^- \rightarrow 2Fe(II) + I_2.$$

and that the iodine produced from this reaction would be sensibly the same in both sample and blank, providing the order of reagent addition was

Sample. (1) alkali/free oxidising agent (2) manganese (3) acid.

Blank. (1) alkali/free oxidising agent (2) acid (3) manganese.

In recent years attention has been drawn to the special case of the ferrous ion (10), (6), (22), (39), (40), (41) which does not appear to act in the above manner.

Wickert (10) states that small quantities of oxygen and small quantities of ferrous iron do not react at the pH of high pressure boiler feed-water but that when made alkaline during the oxygen estimation the oxygen combines with the iron. Young (22) and Potter (6) on the other hand believe that the reaction is of a different form. They hold, as stated by Potter, "When the water under test contains ferrous ion, ferrous hydroxide is precipitated in the sample and reacts with some or all of the dissolved oxygen (this also happens in the blank, but here the reaction is

harmless) the resulting ferric hydroxide dissolves at the acidification stage forming ferric ions, which will not react quantitatively at high dilution with iodide or o-tolidine, etc. Since the blank cannot correct for any dissolved oxygen that fails to be consumed by the Winkler reaction, a low or nil result is obtained.

From the publications of Wickert and Potter it must be taken that these authors found hitherto unsuspected errors when ferrous ions were present in boiler feed - water. These results apparently contradict the findings of Sebald (13) who, as noted earlier, found no interference by ferrous ion when using the A.S.T.M. method. It would appear that the findings of Sebald should be set aside, though admitting the possibility that they may be correct enough for the particular water he was using. Sebald used water obtained from a laboratory deaerator and added the ferrous ion to it under controlled conditions therefore perhaps boiler - water conditions were not duplicated. The significance of this will become apparent when the Cambridge Instrument Company's findings are discussed.

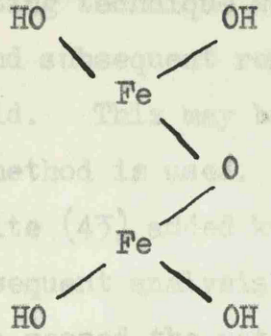
If Wickert was correct, and the ferrous interference came from the reaction between ferrous ion and oxygen, it is then necessary to process both sample and blank out of contact with air in order to minimise the error as it is caused by the ferrous ion - oxygen reaction in the blank. This is mentioned as it is common practice to take little care when processing the blank.

Potter, suggests that the error is partly the result of equilibria involving the ferric ions, causing them to be reduced and hence liberate iodine in differing amounts in the sample and blank. This would be accounted for by the fact that in the sample ferric hydroxide, manganous hydroxide, and manganic hydroxide are neutralised by acid in an iodide solution, whilst in the blank only ferric hydroxide is present

It would have appeared until recently that a synthesis of the two hypotheses would provide a satisfactory reason for the peculiar effect of ferrous ion but in 1958 Cambridge Instrument Company (42) published accounts of tests carried out with a new electrochemical oxygen analyser, described in section 5:3, which gave results at variance with the chemical test method of Potter (6). After a careful examination they concluded that the lack of agreement was due to the fact that the instrument and the chemical tests were not measuring the same thing.

The Cambridge workers postulate the existence of a ferrous oxyhydroxide

compound with a possible structure:-



and attribute the low result obtained on their instrument to this. They reasoned that the "oxygen" measured in chemical methods consisted of free molecular oxygen and oxygen contained in a compound such as the one above, whilst the instrument only measured free molecular oxygen. They demonstrated the possibility of the existence in feed water of such a substance by the fact that such compounds are decomposed at moderate temperatures. They sampled the feed - water before and after a low - pressure heater and obtained the same result from both sources. The chemical method however gave a higher value before the heater but the same value as the instrument after the heater. This result was explained by assuming that ferrous oxyhydroxide was present and had been decomposed on heating to an oxide no longer affecting the chemical test.

$$\begin{matrix} Fe(OH)_2 \\ | \\ O \\ | \\ Fe(OH)_2 \end{matrix} \longrightarrow Fe_2O_3 + 2H_2O.$$

It is obvious that clarification is needed on the question of the effect of metal ions in the analysis of boiler feed - water. The fact that the error can arise from a reaction between ferrous ion and oxygen explains why ferric ion produces no interference. In this case the effect of incomplete reduction is probably cancelled by the "reversed - reagents" technique. However if the Cambridge experience is correct a new approach must be made to investigate whether the "oxygen" measured by the chemical tests is in fact the better estimation of the potential corrosivity of the water.

Wickert (10, 39 and 40) has proposed several methods to overcome ferrous interference. However these methods involve increase in the number of samples taken

and in the number of reagents used and it is doubtful if accurate results could be obtained. One interesting technique was the use of a large excess of bromine water as an oxidising agent and subsequent removal of the excess by the addition reaction with sulphosalicylic acid. This may be a useful technique to deal with interference when a direct chemical method is used.

Potter and White (43) added known amounts of air - saturated water to their samples and, if the subsequent analysis showed a low estimation, ferrous interference was present. They then passed the water through an ion - exchange column to remove ferrous ions.

Potter and White showed that when water of a low oxygen content was passed through an ion-exchange column it was necessary to pass 500 bed volumes of water before the oxygen content of the effluent and the water entering was equal, as there is a gradual desorption of oxygen from the air - saturated water absorbed during regeneration to the almost oxygen - free boiler water. It would appear to be advisable to pass 500 bed volumes before withdrawing the sample although some authors have reported satisfactory removal of interference without mentioning having taken this precaution (44).

Before the apparently successful use by Potter and White of ion - exchange they had attempted to prevent the precipitation of ferrous hydroxide by complexing the iron with fluorides or citrates. They also studied the results obtained when ferrous interference was oxidised by various strong oxidising agents. None of these two procedures proved successful.

The use of ion - exchange has been the most successful method in solving the problem of the ferrous interference.

CHAPTER 5.

THE ELECTROCHEMICAL ESTIMATION OF DISSOLVED OXYGEN.

5:1. DEVELOPMENT FROM POLAROGRAPHY.

The estimation of dissolved oxygen by methods other than purely chemical means has the advantages of providing a continuous record of dissolved oxygen with an absence of analytical manipulation. It is reasonable to assume that an apparatus will eventually be developed on a physical or electrochemical basis to provide an automatic and accurate estimation of the oxygen content of boiler feed - water. However this does not necessarily mean that chemical methods will be outmoded as they are usually employed as checks on the performance of instruments.

The problem has been approached by Laitinen and Kólthoff as an extension of classical polarography and by Todt, who was mainly concerned with the estimation of dissolved oxygen in boiler feed - water. Todt's work is discussed in the next section.

Laitinen and Kolthoff replaced the normal dropping mercury cathode by a stationary platinum electrode and designated this variation as "voltammetry" (45). They found that the limiting diffusion current for oxygen was directly proportional to the concentration of dissolved oxygen present. Giguere and Lauzier (47) confirmed this result.

When this type of cell is used to estimate dissolved oxygen it requires a thermostatic control (45) and addition of an organic substance to suppress the appearance of "maxima effects" on the resulting waves (48). However the introduction of a rotating platinum cathode resulted in the lowering of the temperature coefficient and reduced the "maxima effects" (46). In addition the time taken before the cell came to equilibrium was greatly reduced and an increase in diffusion current observed, but it has been reported that increase in the speed of rotation above a certain rate produces no further exhaltation of the diffusion current (49). No uniformity in the rate of rotation appears in the relevant publications (46, 50, 51).

Another problem associated with this type of work has been interference by mercury from the reference electrode being deposited on the cathode. Giguere and Lauzier (47, 52) among others (56) found this when they used either a saturated calomel electrode or a mercury pool as anodes. This is probably the reason underlying the use of two noble metal electrodes in most commercial instruments and was probably a contributary reason to the withdrawal of an earlier instrument manufactured by the Cambridge Instrument Co.

The pretreatment of metal electrodes has been emphasised by various workers (53, 50, 51, 56). This has been resolved by periodically holding the cathode for 15 minutes at an applied voltage of -0·75 with respect tothe saturated calomel electrode. This results in the direct proportionality between diffusion current and oxygen concentration being reattained. The success of this "ageing" process of the electrodes has been attributed to the reduction of adherent oxygen films on the bright platinum (56)

Measurements of the dissolved oxygen concentration of a 0·1$\bar{N}$ potassium chloride solution were taken while nitrogen was being bubbled through the solution (46). It was found that after 15 minutes 14% of the oxygen remained and after 30 minutes 2% remained. This is of particular interest to the problem of obtaining "oxygen - free" water or reagents as it shows that the oxygen content would fall to 0·2 p.p.m. which would be quite tolerable for Winkler reagents but too high for "deaerated water."

Another significant factor in this work was the observation that when sodium sulphite was added the oxygen wave disappeared after 10 minutes. It is possible that if interfering substances are present that sulphite could be added (providing the interfering substances are not affected by it) and the difference in the currents obtained could be used as a measure of the oxygen content of the solution.

Hydrogen peroxide has been successfully used to increase the diffusion current when dissolved oxygen has been estimated (55) but the use of hydrogen peroxide is severely limited in the analysis of boiler feed - water as it is very rarely that this water would be free of substances which would react with it.

No commercial instruments based on a rotating electrode have been produced but instruments are manufactured in which the same advantages accrue by having stationary electrodes and a flowing solution.

5:2. COMMERCIAL INSTRUMENTS BASED ON IMMERSED ELECTRODES.

Most of the commercial dissolved oxygen analysers are based on German work, principally that of F.Todt. This work was developed from the observation that when certain pairs of metals are immersed in water containing dissolved oxygen a current flows and this current is proportional to the concentration of the oxygen present.

An early apparatus of this type was found in Germany after the 1939 - 45 war and investigated by the Admiralty Materials Laboratory (57, 58). As a result of this work and a study of earlier German publications (59, 60, 61) some British

prototypes were built. With the experiences gained using these and a study of further German publications (62, 63, 64) certain conclusions can be drawn about this type of oxygen analyser. Most of the comments in this section have no published source of reference and relate to the author's conclusions drawn as far as possible from the descriptions issued by the relevant manufacturers (which are naturally exceedingly brief) and personal conversations with other workers in this field.

The underlying theory of this estimation is that when two electrodes are immersed in a solution containing dissolved oxygen a potential difference is setup. Hydrogen gradually builds up on the cathode until the cathode becomes polarized. If no oxygen was present no current would then flow. However with oxygen present the oxygen molecules diffuse to the cathode and are reduced by the hydrogen thus depolarizing the cathode, and a current flows. The magnitude of this current is proportional to the oxygen cconcentration.

Various factors influence this current and have been investigated. Todt (61) reported on the effect of sodium chloride on it. The sodium chloride is used as a supporting electrolyte for the same purpose as it is used in normal polarographic analysis i.e. to carry the current through the solution and as the supporting electrolyte takes no part in the electrode reactions the diffusion currents measured contain no components due to migration currents as;

Limiting current = diffusion current + migration current.

The addition of salt results in an increase in the current produced from the cell. However for a given oxygen value the exhaltation of the current approaches a certain limit beyond which further increase in salt concentration has no effect on the current. Todt (63) used a solution with a salt concentration of 500 mg.of Na Cl/litre and Grubitsch (65) used 0·1 N sodium chloride. Todt's concentration is the one usually used.

Increase in the solution agitation increases the current, since the rate at which the oxygen reaches the electrode increases; which means that when a continuous reading apparatus is used, for dissolved oxygen determinations, the rate of flow of the water past the electrodes must be controlled. This is usually obtained by capillary tubing allied to constant head devices.

The temperature coefficient of the cell has been found to be about + 2% per ^{o}C in the range 18^{o} - 28^{o}, necessitating the use of temperature control (58).

When this type of apparatus, hereafter referred to as the "immersed-electrode" type, is used with pure water excellent results are obtained, but in water containing impurities, such as are present in boiler feed-water, certain inherent faults appear.

Most of the commercial immersed-electrode analysers are calibrated by obtaining a zero reading (see later discussion) and then producing gradually increasing known amounts of oxygen, in the feedwater to enable a graph of oxygen concentration against diffusion current to be drawn up. The oxygen is usually produced by a small electrolytic cell in the feed line prior to the measuring cell so that, knowing the applied current and the water flow rate the increase in oxygen concentration of the water may easily be calculated.

If reducing agents are present some of this oxygen, being extremely active, is reduced as it is formed. Thus less oxygen than is calculated will be added to the water and will result in an incorrect calibration graph. The amount of oxygen used up in this way is difficult to assess. This error can be avoided by adding known amounts of air-saturated water to calibrate the instrument. It is of interest to note that recently one meter of this type has been modified to incorporate a calibration unit to enable the calibration to be carried out by addition of air-saturated water.

The effect of impurities in the feed water can introduce a major error in the measurement cell. The cathode is at such a potential that the reaction

$$H^+ + e \rightarrow H\ (gas)$$

takes place. This potential depends on the material of the cathode and the nature of the solution. The cathode material is usually chosen so that the potential at which the above reaction takes place is about + 0·5 volts (66). However at this potential reactions, other than the reduction of oxygen, can take place producing currents which add to that produced by the oxygen reduction. Some of these interfering reactions can be caused by the presence of cuprous ions, a certain ratio of $\frac{Fe(III)}{Fe(II)}$, ammonia, sulphite, and probably hydrazine (66). In addition it is quite probable that undetected interference from organic sources can occur.

It is usually stated that the current caused by interfering substances can be overcome during the calibration of the apparatus. However many of the commercial instruments for which this claim is made cannot do this. The usual analogy is that

drawn from polarographic analysis when the diffusion current measured in this case is the sum of the current due to the reduction of an interfering ion (which reduces at a potential prior to the half wave potential of oxygen) plus the diffusion current due to the oxygen,

$$\text{i.e. } I = i_{\text{interference}} + i_{\text{oxygen}} . \quad \text{——} \quad (1)$$

Now if an inert gas is bubbled through the solution the oxygen is removed and a current, I^1 is obtained and,

$$I^1 = i_{\text{interference}} \quad \text{——} \quad (2)$$

therefore (1) ——(2) should give the current due to oxygen alone. This is correct but it implies that both measurements must be done under the same conditions of flow etc. To do this correctly either an oxygen scavenger, which does not affect the measuring cell, must be added to the feedline before the cell, or the feed-water should be scrubbed with an inert gas to remove all oxygen, again before the measuring cell, and the feed-water flow in both these cases must be kept constant.

It is understood that one commercial instrument is presumed to allow for interference by shutting off the water flow and, with the electrodes in circuit, waiting until all the oxygen in the water is reduced and using the current then recorded as "zero". Two errors may occur here, (a) some of the interfering agents are used up by reaction at the electrode and so the residual current does not include all the current due to the interference, and (b) as there is no flow it cannot give a true representation of the residual current when the water is flowing past the electrodes.

Another disadvantage inherent in the immersed electrode analysers is that when boiler feed-water is used the electrodes become fouled by the impurities in the water. This necessitates taking the electrodes out to clean them, and also brings in possibilities of errors when the fouled electrodes are working. One method that has been used is to circulate fine grit continually to abrade the electrode surface. This may however have the effect of keeping the electrode surface very sensitive and errors may result as many workers on "voltammetric" methods, described in Section 5:1., have emphasised the necessity of "ageing" the electrodes before accurate results are obtained.

5:3. OTHER COMMERCIAL INSTRUMENTS.

The method of Czuha and Thayer (67) involves the conversion of nitric oxide to nitrogen dioxide by passing the nitric oxide through boiler feed-water containing oxygen. The dioxide dissolves and the increase in conductivity is related to the oxygen content of the feed-water.

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

At the prevailing dilution no significant error is caused by taking the increase in conductivity to be due wholly to nitric acid.

The incoming feed water is passed through a mixed bed resin which converts cations to H^+ and anions to nitrate ions. It then flows via a conductivity cell into a scrubbing column where it is saturated with nitric oxide after which it flows through another conductivity cell. The difference in the two conductivities gives the rise in nitrate concentration i.e. a direct measure of the oxygen content of the solution.

The zero is obtained by stopping the flow of nitric oxide and waiting until the differential conductivity is nil. The scale is then calibrated by producing oxygen in the water by electrolysis, which may give rise to errors if all reducing agents have not been removed by the resins.

A report on this analyser (68) recommends that the complicated valve circuitry be simplified to enable certain operations to be non-automatic thus reducing leakages without adding greatly to the human participation in the analysis. The instrument is reported to be satisfactory in the range of dissolved oxygen quantities found in boiler feed-water although neither the accuracy or precision is given.

The principle of this method appears sound and the only dubiety arises in the performance of the resins with regard to the impurities present in feed water. No great detail is given on this point

One method of overcoming the problem of interfering agents is to remove the oxygen from the water and transfer it to a measuring cell. In the Baker-Hersch meter (69, 70) the oxygen in the water is displaced by a stream of "oxygen-free" hydrogen in a scrubbing tower. The oxygen/hydrogen mixture then passes into a patent dry-cell arrangement which produces a current proportional to the oxygen content of the

gas. This type of arrangement solves the problem of interference as obviously it does not matter what impurity is present in the water providing it is not displaced by the hydrogen.

The zero of the instrument is obtained by passing pure hydrogen through the measuring cell and the scale calibration is carried out by adding known amounts of electrolytically generated oxygen to the gas stream. This can be related to the oxygen displaced from the feed water by a knowledge of the relevant flow rates and partition coefficients.

The measuring cell consists of a silver cathode and an activated cadmium anode, the electrodes being separated by a porous tube saturated with potassium hydroxide (71). A temperature regulator is incorporated in the system.

The author has had no personal experience of this instrument but, the theory being rational, there must be operational difficulties which have prevented this instrument having been widely accepted. It is understood that one difficulty is that the measuring cell suffers interference by impurities in boiler feed water being carried into it by the carrier gas. One of these interfering substances is said to be ammonia which attacks the electrodes.

Cambridge Instrument Co. have recently developed an automatic electrochemical dissolved-oxygen analyser, a simplified drawing of which is shown in fig. (2). Hydrogen (purified by passing through furnace F_2) sweeps out the oxygen in the feed-water and the resultant mixture bubbles into the measuring cell until the recirculating buffer solution eventually comes into equilibrium with it. A galvanic current is produced by reactions at the immersed platinum black and gold electrodes. This current is proportional to the oxygen content of the buffer solution. The zero of the apparatus is obtained by cutting off the water flow, passing hydrogen and taking the resulting gas mixture to the measuring cell via furnace F_1. The current falls as the oxygen content of the cell solution decreases and the minimum steady current is taken as the instrument zero. This does not introduce the errors discussed previously as the flow conditions in the measuring cell are unaffected although the feed-water flow has ceased.

The scale is calibrated by introducing known amounts of oxygen into the gas mixture coming from the scrubbing tower when the instrument has been zeroed.

The instrument is said not to need a temperature regulator as when the ambient temperature rises the decrease of solubility of oxygen in the measuring cell is compensated by the temperature coefficient of the cell system.

As with the Hersch analyser interference can only be caused by volatile constituents in the feed-water. Ammonia, hydrazine, filming amines, cyclohexylamine, sulphite, and other feed-water conditioners have been introduced into the water in the scrubbing tower with no effect.

On introduction this instrument met severe criticism due to its slow response and the low results often obtained compared with chemical checks. It is understood that in most cases the chemical-test procedure was at fault (42, 72).

CHAPTER 6.

CALIBRATION OF THE O-TOLIDINE METHOD.

6:1. INTRODUCTION.

Schumann in 1954 (15) outlined the advantages arising from the use of cerium salts in the Winkler reactions. This has been discussed in section 2:2.. Initially it was thought that difficulties might arise during the potentiometric estimation of iodine and it appeared expedient to have a convenient standard enabling the efficiency of the preliminary deaeration test-apparatus to be estimated. The method devised also predicts the limit of the cerium/o-tolidine method when conventional apparatus is used.

The determination of dissolved oxygen with cerous salts and o-tolidine depends on the undernoted reactions.

(a) $Ce\ (III) + 3\ OH^- \longrightarrow Ce\ (OH)_3$.

(b) $Ce\ (OH)_3 + O_2 \longrightarrow Ce\ (OH)_4$.

(c) $Ce\ (OH)_4 + H^+$ + o-tolidine (colourless reduced form) $\longrightarrow$
Ce(III) + o-tolidine(yellow oxidised form).

The final yellow coloured solution produced in reaction (c) is estimated colorimetrically and gives a measure of the dissolved oxygen.

Standard ceric solutions representing a range of dissolved oxygen values were prepared. A calibration curve was constructed by measuring the depth of colour developed by the oxidation of o-tolidine by the ceric solutions.

Water used in the Experiments.

The water used in all the experiments detailed in this thesis was purified by distillation then passage through a mixed-bed ion-exchange resin (A.R.grade). This was found necessary because of aerial contamination.

6:2. PREPARATION OF STANDARD CERIC SOLUTIONS.

Ceric sulphate (low in other rare earths) was boiled in approximately 3$\bar{N}$ sulphuric acid for 4 hours. This ceric sulphate left only a small residue of undissolved material. The solution was filtered hot and allowed to cool. The cold solution was roughly standardised with sodium oxalate and the concentration adjusted to about 0·13 $\bar{N}$. This 0·13 $\bar{N}$ solution was stored in a dark cupboard for a

week then filtered twice through small pore filter paper. The filtered solution was accurately standardised with sodium oxalate.

Sodium oxalate (A.R.) was dried at 120°C. Small amounts were abstracted when needed and cooled in a desiccator. From this the amount necessary to give a titre of 10·5 - 11·5 ml. was weighed into a 250 ml. beaker and approximately 130 ml. of 3$\bar{N}$ sulphuric acid added. The solution was stirred with a magnetic stirrer and when the oxalate was dissolved, 10 ml. of the ceric sulphate was added from a grade A pipette. If at any stage a white precipitate formed, some concentrated sulphuric acid was added. This prevented the formation of the basic sulphate.

The titration was completed with a 2 ml. burette (grade B calibrated with distilled water). When the solution first turned yellow it was heated to 60°C. and the colour disappeared. The titration was continued at this temperature until the first permanent yellow colour. A blank titration was performed at 60°C. using the same volume of dilute acid. This blank titre was subtracted from the original.

6;3. CONSTRUCTION OF STANDARD CURVE.

The absorption curve of the yellow oxidised o-tolidine solution was plotted using a "Unicam" spectrophotometer (result table 1 and fig. 3) and the optical densities of the range of yellow solutions were obtained with a Hilger "Spekker" long-cell sbsorptiometer. Kodak filter No.1 was used with the absorptiometer as its spectral absorption curve corresponded to the absorption peak obtained with the "Unicam". 4 cm. or 20 cm. cells were used in the "Spekker" depending on the depth of colour of the solutions.

Reagents.

(a) Ceric sulphate prepared and standardised as described.

(b) 0·4g. of o-tolidine (A.R.) dissolved in 100 ml. of 0·1 $\bar{N}$ hydrochloric acid (A.R.)

(c) 50% sulphuric acid.

1 ml. of the standard ceric sulphate was diluted to 1 lr. with 2 $\bar{N}$ sulphuric acid. This is solution A. Appropriate amounts of solution A were taken and diluted. Sulphuric acid and o-tolidine were added to these diluted solutions and the developed colour measured in the "Spekker." 1·3 ml. of reagent (b) and 5 ml. of reagent (c) were added for each 250 ml. of final solution. The results and curves appear in table 2 and fig. 4.

A straight line relationship was obtained and both the 20 cm. and the 4 cm. cells resulted in lines which intersected the x-axis in the region corresponding to 0.002-0.003 p.p.m. of dissolved oxygen. The graph shows that the maximum divergence from the lines is approximately 0.001 p.p.m. No explanation is offered for the greater divergence of the 0.074 p.p.m. result appearing in table 2. Fig.4 and table 2 show that although the lower limit of measurement, with this apparatus, appears to be equivalent to 0.002 p.p.m. of dissolved oxygen there is adequate discrimination between two values differing by 0.0025 p.p.m. This suggests that the calibration could be employed in dissolved-oxygen measurements below 0.0025 p.p.m. since the A.S.T.M. "reversed-reagents" method, for example, depends on a subtraction of a "Sample" and "Blank" which have both had oxidising agents added to them. The optical densities of these solutions could be estimated from the graph on fig.4 as the amount of oxidising agent added is usually greater than a quantity equivalent to 0.003 p.p.m. of oxygen.

Effect of pH.

A solution equivalent to 0.04 p.p.m. of oxygen was prepared in the manner described above. The final colour was developed in 100 ml. flasks to which differing amounts of 1:1 sulphuric acid had been added. The results (table 3) demonstrate that the depth of colour is sensibly independent of acid concentration.

Colour Stability.

A solution was prepared and the yellow colour developed. This was put into a 4 cm. cell and frequent readings were taken over a period of 6 minutes. The results(table 4) show that no significant deterioration takes place in this period. It was found that the o-tolidine had to be added to the dilute ceric solutions immediately as the latter deteriorated rapidly in the laboratory atmosphere.

6:4. DISCUSSION.

When these tests were first attempted no colour could be obtained when low concentrations of Ceric solutions were used. This was attributed to impurities in the o-tolidine (29) or reducing agents found in the laboratory

distilled water.

The o-tolidine was purified in the manner described by Haslam and Moses. This is essentially a method in which the tri-acetyl derivative is prepared and subsequently hydrolised to give purified o-tolidine. Use of reagent thus purified did not improve the results.

Improvement only became evident when the distilled water was purified by passage through a mixed-bed ion-exchange resin (A.R.).

Experimental Error.

It is usually considered that the method chosen to find the end point of the sodium oxalate/ceric sulphate titration, i.e. without an indicator, is inaccurate. However as the solutions used were highly diluted this error becomes negligible. As the blank values were about 0·05 ml. it is safe to assume that the standardisation titration is not more than 0·10 ml. from the true value. This would produce less than a 1% error in the standardisation giving rise to less than 1% error in the final standard curve shown in fig. 4. This is quite tolerable in the present work.

CHAPTER 7.

EARLY DEVELOPMENT OF APPARATUS.

7:1. PRINCIPLE OF METHOD.

The literature study showed that misleading conclusions regarding the overall accuracy of an analytical method can be made if only one aspect of that method is studied. For example, it is of doubtful value to devise a very accurate estimation of iodine released during dissolved oxygen determinations without consideration of the factors controlling the release of that iodine. Therefore in the present work the principle adopted was to obtain "oxygen-free" water, inject a known volume of air-saturated water and use "oxygen-free" reagents. If the method proved satisfactory in pure water the effects of known reducing agents could then be studied. In this way the effect of any interference can be easily assessed.

The specified accuracy was to be within 0·003 p.p.m. of the true oxygen values.

7:2. REAGENT DEAERATION.

In the preliminary tests the reagents were deaerated by modifying Verbestel's technique (73, 74). A simplified form of Verbestel's arrangement is shown in fig. 5. It was considered impossible to dispense reagents with the accuracy required in dissolved oxygen estimations by breaking the glass capsule on tightening the screw clips. It was also found difficult to obtain a vacuum using the thick plastic tubing recommended.

The apparatus shown in figs. 6 and 7 was then evolved. The polythene/glass capillary seal was made by melting the polythene bottle neck and alternately pressing and twisting it on to the capillary.

The apparatus in fig. 6 was evacuated by a water filter pump and filled with nitrogen three times. During evacuations the reagent was stirred by a magnetic stirrer which assisted the release of dissolved gases. After the third filling with nitrogen the conical flask was inverted around standard joint M and the reagent ran into the B.55 tube. Another evacuation and filling with nitrogen transferred the reagent to the polythene capsule. The full capsules were taken out, the capillaries sealed off, and stored until needed in boiled water under an oil seal.

The reagent syringes were flushed with the nitrogen flowing through the

glass tube shown in fig. 8. The plunger was finally drawn up past the zero mark and the syringe withdrawn. It was then inserted through a polythene reagent capsule. When the plunger was depressed the increase in pressure inside the capsule allowed the syringe to fill as the plunger was slowly withdrawn.

The needles were of the "side-hole" type as ordinary needles were blocked by the polythene.

7:3. TRANSFER OF DEAERATED WATER TO REACTION VESSEL.

Water contained in the round-bottom flask in fig. 9 was deaerated by evacuation. These methods are detailed in the next section. In all cases after the final evacuation the apparatus was filled with nitrogen and joint T disconnected. Joint T was then connected by glass tubing to the water entry limb of the reaction vessel (fig. 10). The sleeves on the glass tubing were made by covering the butted ends with thin p.v.c. tubing. A B19 brass stirring gland of the stuffing box type was located in the standard joint of the reaction vessel and a link stirrer was fitted through the stirring gland. The vaccine caps of the reaction vessel were boiled in saturated sodium carbonate then distilled water. This served to remove the more readily soluble impurities.

After the reaction vessel was coupled to the flask containing the deaerated water it was evacuated, filled with nitrogen then filled with deaerated water. To accomplish this taps L and N in fig. 9 and the waste outlet and nitrogen inlet of fig. 10 were all closed. The stirrer gland was tightened and with the water inlet to the reaction vessel open, the apparatus was evacuated by a pump connected to the nitrogen outlet. After evacuation the apparatus was filled with nitrogen and, as the stirring gland was inefficient as a vacuum seal, nitrogen was passed out via the waste outlet for 2 hours.

The deaerated water flask was now inverted around joint P and nitrogen passed through tap L, displacing the water into the reaction vessel. The reaction vessel was filled to the graduation mark and nitrogen passed over the surface throughout the estimations.

7:4. INJECTION OF REAGENTS.

After filling with reagent as described in 7:2., the excess reagent was ejected from the syringe and the needle pushed through one of the vaccine caps in the reaction vessel. The needle was pushed into the body of the solution and the

reagent injected. The cerous/o-tolidine method proposed by Schumann (15) was used for the estimations and the oxygen value of the solution obtained from the cerium/o-tolidine standardisation curve (section 6:3.).

7:5. PREPARATION OF "OXYGEN-FREE" WATER.

The various methods available to prepare "oxygen-free" water are:-

(a) Freezing the water and evacuating with a high vacuum pump. Dissolved gases are released as the ice melts and after these have been pumped off the process is repeated (75).

(b) Evacuating the apparatus by a water jet pump, allowing the solution to come to equilibrium with nitrogen, then repeating the process (73, 74).

(c) Evacuation as described by Heidt (76).

(d) Bubbling nitrogen through the water for 24 hours (29).

(e) Boiling the water with continuous passage of nitrogen.

(f) A combination of any of the above methods.

Methods (a) and (d).

The apparatus in fig. 9 was used to test the high vacuum techniques. A residual of non-condensible gases giving a pressure of 10^{-5} mm. was obtained by Good and Purdon (75) after four cycles of method (a). This method was attempted but was found to be impracticable as the freezing and melting cycle took 1 - 2 hours. The time factor also ruled out method (d).

Method (c).

To test method (c) a 1 lr. flask was connected between tap M and joint T of fig. 9. This 1 lr. flask was evacuated with tap N closed then tap M was closed and N opened. This gradual evacuation was repeated until the gauge pressure was equal in the two flasks. Vacuums of 10^{-2} mm. (the limit of the pump) were obtained. Heidt (76) reached pressures of 10^{-3} - 10^{-5}mm. Stirring the water (magnetic stirrer) facilitated the release of dissolved gases. After the flask containing the water had been deaerated it was filled with nitrogen and disconnected at joint T. It was then inverted and the water transferred to the oxygen measuring apparatus in fig. 10.

The method was abandoned as it gave a high oxygen residual and involved difficulties in manipulation.

Method (b)

The water was deaerated by a repeated cycle of evacuation and filling with nitrogen. The apparatus in fig. 9 was used and since a water filter pump was used

for the evacuations the vapour trap was unnecessary. The water was continually stirred by a magnetic stirrer. After 3 evacuations the water was transferred to the reaction vessel as described. This method showed residuals of 0-0·020 p.p.m. of dissolved oxygen.

After this result it was obvious that a more rational apparatus should be designed as the manipulation involved during the inversion of the deaerated water flask led to repeated breakage of tap N. The results proved unsatisfactory but the reservation is made in that this may be due to apparatus defects.

Method (e)

Water was boiled for one hour with nitrogen passing ttrough it continually. This was done in the apparatus shown in fig. 11. Nitrogen was kept flowing until the water cooled, then the flask was inverted and the reagents injected. This time in four tests two showed no yellow o-tolidine colour, one gave an oxygen value below 0·010 p.p.m. and one was above 0·010 p.p.m.

It was therefore decided that the deaeration method used in the final apparatus would be based on boiling and continuous passage of nitrogen.

7:6. OBSERVATIONS.

Holland (77) in 1959 advocated the estimation of dissolved oxygen by reagent injection with hypodermic syringes. He used a submerged bottle and fitted a vaccine cap on to the filled bottle whilst it was submerged. The reagents were injected through this vaccine cap.

Holland, to minimise the oxygen introduced with the reagents, used 0·05 ml. of each reagent for a 500 ml. test sample. He states however that with oxygen concentrations greater than 0·020 p.p.m. it would be necessary to use larger reagent volumes. In this case the reagent deaeration and injection procedure described in this chapter might prove useful in reducing the oxygen value of the reagents. No difficulties were encountered with this reagent deaeration procedure.

CHAPTER 8.

FINAL FORM OF APPARATUS.

The approach to the problem of the estimation of dissolved oxygen was outlined in section 7:1. The first requirement was a satisfactory method of deaerating water, and the work on this aspect of the estimations showed that the most practicable method was to pass nitrogen continuously whilst boiling the water.

8:1. SAMPLING PROCEDURES.

The sampling vessels most commonly used when this work commenced were the McLean tube and the "submerged-bottle". The A.S.T.M. (7) refinement of the McLean tube is shown in fig. 12(a). The reagents are added by filling end "A" to the required level (in the A.S.T.M. tube allowance is made for the volume of the tap bore), opening the top tap then partially opening the other tap. The Water Pollution Laboratory (19) tube in fig. 12(b) facilitates the filling and cleaning of the reagent entry tube as the excess is run to waste when the level of the reagent is brought down to the graduation mark.

Experience with this type of tube soon showed that it was difficult to keep the hydroxide precipitate in a state of suspension. When the acid reagent was added excess precipitate was displaced from the tube and hydroxide precipitate formed in the bores, making them extremely difficult to clean. Addition of strong sulphuric acid solution (3:1) to dissolve the manganese hydroxide resulted in a violent reaction taking place with the release of iodine from the alkaline-iodide remaining in the tap bores. It has been stated (19) that this has been ameliorated by the substitution of phosphoric acid in place of sulphuric. However this would not affect the other disadvantages found and a more satisfactory reaction vessel was sought.

The submerged-bottle technique illustrated in fig. 12(d) is much favoured by German workers. The apparatus is very simple as it consists only of a bottle with a well fitting stopper and a pipette, by means of which the reagents are added under water. It is probably safe to assume that oxygen does not diffuse through the constantly replenished layer of deaerated water between the top of the bottle and the atmosphere during the processing of the sample, if, as is common practice, the tube from the deaerated water supply is left in the overflow vessel throughout the processing.

It was decided that this method would be suitable for the analysis of air-

saturated water but would not be satisfactory for the proposed low oxygen value measurements as there would always be a certain doubt about the accuracy and precision in dispensing air-saturated water and the various reagents into the bottle.

During the present work details of two sampling procedures involving vessels and techniques superior to the above have been published by Young (22) and Potter (6). These appear in figs. 13 and 12(c). Potter connects the sample water supply to the capillary side-neck and with the stopcock uppermost and the ground glass cone turned through 180 degrees from the position shown, fills the tube. The flask is then turned as illustrated and, after flushing the reagent side-neck to waste with the first reagent, the capillary is completely filled with reagent. The ground joint is rotated until the hole is open to the capillary side-neck and on opening the stopcock the reagent is drawn into the tube. The capillary side-neck is calibrated so that the volume of reagent run in is 0·125 ml. This tube is now widely used in power stations.

Young's apparatus was designed to take warm water samples as he believed more favourable reaction conditions were obtained. The reagents are added with a nitrogen stream passing over the surface of the liquid. This arrangement allows the liquid to contract without subsequent atmospheric contamination.

Potter (5) describes a variation of his sampling tube in which the bottom stopcock is replaced by a ground glass piston arrangement. The piston is withdrawn as the reagents are added to the sample and this overcomes theneed to expel an amount of the test solution equivalent to the volume of reagent added and it can also be used for warm water samples.

8:2. DESIGN CONSIDERATIONS.

The A.S.T.M. "Referee Test for Dissolved Oxygen" (6) was selected as the basis of the initial standardisation of the proposed apparatus as it is the synthesis of the work of various authors during the last 20 years. This test requires a 500 ml. sample. This volume was retained in preference to a smaller volume, as it allows larger volumes of air-saturated water and reagents to be used with a corresponding decrease in the accuracy required during the additions. The A.S.T.M. sampling flasks have to be flushed ten times before a correct sample is adjudged to have been collected. This would have entailed deaerating at least ten litres of water and it would have been necessary to allow about two hours to boil this volume of water. The alternative

was to have a continuous supply of boiling water but for various reasons this was not possible. These objections also apply to the "submerged bottle" technique.

Another design factor to be considered was the injection of the reagents. From the discussion in section 8:1. it can be seen that the extant sampling vessels were not felt to be satisfactory. The apparatus required was one which would enable deaerated reagents to be injected in such a manner that one reagent would not form precipitates by reaction with another at the point of injection.

The final design of the apparatus used is shown on figs. 14 - 19. It was constructed of "Pyrex" glass.

This apparatus requires the boiling of only two litres of water for the analysis of a sample and blank of 500 ml. each. The reagents are added through separate entries and the rate of addition may be varied as desired. The glass float (fig. 18) minimises the diffusion of oxygen from the solution under test to the atmosphere above and permits the addition of reagents without displacing the solution to waste. The diffusion of reagents and air-saturated water into the test solution is reduced by making the connections of 1 mm. bore tubing.

The final consideration in the design of the apparatus was to have the apparatus self-contained so that all the operations, except the final titration, could be carried out by manipulation of stopcocks and there would be no need to move parts of apparatus from one position to another. This, it was hoped, would minimise both breakage and the possibility of atmospheric contamination.

8:3 DESCRIPTION OF APPARATUS.

The apparatus (fig. 19) can be simply described as consisting of a deaerator (the 2 litre flask) from which "oxygen-free" water is taken into a reaction vessel fitted with tubes from which "oxygen-free" reagents are dispensed. A full description of this procedure is given in the next chapter.

A small thermometer is placed inside the tube connecting the cooler to the reaction vessel.

When the apparatus is assembled p.v.c. and rubber sleeves are fitted to the tube ends, the rubber sleeves to gas lines only. The nitrogen washing-train is sealed with picien wax (fig.15.)

The deaerating flask (fig.16) is partially enclosed by a "sindanyo" box with a metal base, preventing breakage through overheating with the bunsen.

All taps are "high vacuum" grade.

The reaction vessel is stirred by a magnetic stirrer.

8:4 IODINE TITRATION.

The various methods for analysis of iodine detailed in the review section were assessed and it was concluded that, as pure water was to be used in the experiments, and that each result could be checked as it was obtained by comparing the oxygen added with the oxygen measured, a normal potentiometric titration could be used. This method was adopted with the reservation that more refined electrometric methods would be used if it proved unsatisfactory but it proved successful. The only difficulty encountered was poisoning of the platinum electrode, detailed in section 9:5, and during one series of tests (not reported) when the efficiency of a deaerator, which was deaerating untreated tap-water, was being estimated. In the latter case random titres occurred when it was impossible to obtain steady potentials. This was attributed to impurities in the raw water.

The titrations were carried out in a spoutless beaker under a nitrogen atmosphere. Fig. 20 shows the titration assembly.

The tubes passing through the "sindanyo" cap in fig. 20 were located with split rubber tubing. The salt bridge arrangement reduced contamination of the calomel electrode as, when the beaker was withdrawn after each titration, a slow siphoning flushed out the sintered salt bridge.

The instruments used were a Pye "Universal Precision Potentiometer" and a Cambridge "Spot Galvanometer".

The titration assembly was tested by titrating 500 ml. of acidified iodine solution with 0·005$\bar{N}$ sodium thiosulphate. The end-point of the titration was located by the method of Hostetter and Roberts (78) which necessitates the addition of equal increments of reagent. The solution was stirred by a magnetic stirrer.

Preliminary titrations were carried out to determine the optimum increment. A typical result is shown below.

Reagent added (ml.)	Potential (E) (volts)	dE	d^2E.
0.40	0·4046		
		13	
0·42	0·4033		- 50
		63	
0·44	0·3970		- 237
		300	
0·46	0·3670		+ 104
		196	
0·48	0·3474		+ 97
		99	
0·50	0·3375		+ 34
		65	
0·52	0·3310		

$$\text{End point} = 0{\cdot}44 + 0{\cdot}02 \left(\frac{237}{341}\right)$$

$$= 0{\cdot}455 \text{ ml.}$$

The same results were used to find the end-point assuming 0·04 ml. increments. Four such comparisons are given below:-

End-point with 0·02 ml. increments. (ml.)	End-point with 0·04 ml. increments. (ml.)	Difference. (ml.)	Difference as p.p.m. of O_2.
0·44	0·445	+ 0·005	+ 0·0004
0·455	0·46	+ 0·005	+ 0·0004
0.46	0·465	+ 0·005	+ 0·0004
0·455	0·46	- 0·005	- 0·0004

The normal procedure was to add 0·04 ml. increments reduced to 0·02 ml. in the region of the end-point. The above table shows, however, that acceptable results are obtained even with 0·04 ml. increments.

The burette tip was raised out of the solution after each addition otherwise

the potentials were influenced by diffusion of the reagent into the solution.

Stirring was continuous throughout the titrations.

CHAPTER 9.

THE ESTIMATION OF MICRO QUANTITIES OF OXYGEN DISSOLVED IN PURE WATER.

9:1. REAGENTS.

Alkaline potassium iodide. 700 g. KOH (A.R.) and 150 g. KI. (micro analytical specification) made up to 1 lr.

Iodine solution. 0·1$\bar{N}$ (prepared from resublimed iodine).

Alkaline iodide/iodine solution. A small volume of the 0·1$\bar{N}$ iodine was made up to 100 ml. with the KOH/KI solution. To assess whether the iodine concentration was correct an A.S.T.M. blank estimation was carried out. If the final titre was below 0·10 ml. of sodium thiosulphate the solution was acceptable.

Sodium thiosulphate. A 0·1$\bar{N}$ solution was prepared as a stock solution. This was diluted to 0·005$\bar{N}$ before each test.

Manganous sulphate. 480 g. $MnSO_4 . 4H_2O$ (A.R.) made up to 1 lr.

Sulphuric acid. 750 ml. H_2SO_4 (A.R.) diluted to 1 lr.

All of the above reagents were prepared as specified by the A.S.T.M.(7).

Although many authors have taken extreme care in standardising the stock solution of sodium thiosulphate daily it was found that the normality did not change before the solution was finished. In fact it was found that when A.R. grade sodium thiosulphate was used the calculated normality did not differ from the value found when it was standardised with potassium iodate. Typical figures were:-

Normality of thiosulphate (a) by weight = 0·0997
(b) by standardisation = 0·0993.

The thiosulphate was however standardised when each new stock was prepared. Young reached the same conclusion (20).

The graduated glassware used in the experiments was calibrated with distilled water. 1 ml. or 2 ml. grade B burettes were used depending on the range of dissolved oxygen under investigation. Similarly a 1 ml. "Tuberculin" syringe or a 2 ml. "Chance" syringe were used to inject the air-saturated water. The reagent side necks were graduated by marking the levels at which 2 ml. of distilled water were delivered.

Vanadous sulphate. (79)

The vanadyl sulphate in the gas washing train (fig.15) was reduced with Hg/Zn amalgam (both A.R. grade) then quickly transferred into the wash bottles which

contained fresh amalgam. The vanadyl sulphate was initially reduced with zinc dust but it was found that hydrogen sulphide, which interfered with the analysis, was slowly liberated from the solutions. This gas presumably came from sulphide impurities in the zinc dust.

9:2. AIR-SATURATED WATER.

The air-saturated water injected into the deaerated sample was prepared by bubbling clean compressed air through a sintered disc (porosity 3) which was inserted at the bottom of a 15 litre aspirator bottle full of demineralised water. The water was continually stirred at 20 r.p.m. by a mercury sealed stirrer. The water flowed under gravity from the aspirator to the injector syringe.

9:3. EXPERIMENTAL PROCEDURE.

Before the initial estimation nitrogen was passed for 24 hours through the gas washing train.

The following description of the procedure is written with reference to fig. 19.

DEAERATION OF WATER AND REAGENTS.

The water in the 2 lr. flask was heated while nitrogen was passed through it. The remainder of the apparatus was isolated by taps 1 and 3 and the other taps turned to allow the reaction vessel, capillary side-tubes, reagent tubes, cooler and the manifold to be evacuated by a water-jet pump. During this evacuation the reagents were introduced, one at a time, to their respective tubes by immersing the waste limbs of taps 7 in small beakers containing each reagent, and turning tap 7 to allow the reagent to fill the tube. The vacuum was now shut off and by adjustment of tap 1 the 2 lr. flask was by-passed and the evacuated portion of the apparatus was filled with nitrogen. This evacuation and filling with nitrogen was performed three times.

After suitable adjustment of taps 7, 8, and 9, nitrogen passed through the reagents, displacing dissolved oxygen, and simultaneously through the reaction vessel. It was found that 15 minutes passage of nitrogen reduced the oxygen content of the reagents to a value not detectable by the A.S.T.M. method. In addition to its displacement by nitrogen, the removal of oxygen was probably accelerated by the fact that when the reagents emerged from the waste limb of taps 7 into the reagent tubes which were under reduced pressure, there was a considerable release of dissolved gases. After the reagents were rendered "oxygen-free" the reagent tubes were isolated and

nitrogen was simultaneously passed through the reagent vessel and the water in the two litre flask.

This latter process continued until the water in the flask was boiling, when the nitrogen flow was altered so that the gas flowed for 5 minutes through the boiling water via taps 1 and 3 and flushed the tube between tap 3 and the 2 litre flask. The taps were now adjusted to pass nitrogen for 15 minutes once again through the boiling water and the reaction vessel. The heating was then stopped.

By this sequence of operations nitrogen always flushed air into a part of the apparatus from where it was subsequently displaced.

Concurrent with the above operations air-saturated water was taken from the bottom of the 15 litre bottle and the flow split into three tubes each with an equal flow rate. Two of the tubes led to the bottom of two 100 ml. standard flasks and the third was connected to the horizontal limb of tap 6. The standard flasks were placed in gas jars which were in a large porcelain trough. The syringe piston was removed and the air-saturated water flowed through the syringe until at least 600 ml. of air-saturated water had run through each standard flask. Tap 6 was then turned until about 3 ml. of air-saturated water flowed through the 1 mm. connecting tube to the reaction vessel, then altered to allow the water again to flow through the syringe. The flow was then terminated, the flasks stoppered, and the syringe piston inserted.

In this way a uniform sample of air-saturated water was obtained having a dissolved oxygen content corresponding to that contained in the syringe. In addition, by following this procedure, the tap bore and capillary connection to the reaction vessel were also filled with this water.

The surplus air-saturated water at the bottom of the reaction vessel was blown out through tap 5 by nitrogen, care being taken that nitrogen still bubbled through the gas traps of taps 9 and 2. When the steam in the 2 lr. flask had condensed some deaerated water was allowed to flow into the reaction vessel via tap 3, the cooler, and tap 4. While this operation was being carried out nitrogen was kept bubbling through the gas trap of tap 2 and displaced through the trap of tap 9 by the water entering the reaction vessel. This water was now blown out of the reaction vessel in the same manner as the surplus air-saturated water.

The partial flushing of the reaction vessel with deaerated water was performed three times and this was sufficient to clear the vessel of the last traces

of air-saturated water.

Collection and Processing of Sample.

Adjustment of the nitrogen and water flow transferred 500 ml. of deaerated water to the reaction vessel, via the cooler, with a final temperature of 20°C. The reagent levels were adjusted to the zero mark, under nitrogen, by adjusting taps 8 and 7 and allowing the excess to flow to waste. The syringe was also adjusted to zero by allowing the excess to flow to waste. The p.v.c. tube on the waste limb of tap 6 was then clipped to prevent leakage of air-saturated water during the injection when the 3-way tap was turned. Nitrogen was kept passing out of tap 2 throughout.

The magnetic stirrer was switched on and the appropriate amount of air-saturated water injected into the reaction vessel followed at three minute intervals by displacement of 2 ml. of each reagent into the vessel by nitrogen pressure. The acid was added slowly to reduce the possibility of iodine release from the potassium iodide. The order of addition was alkaline iodide/iodine, manganese and acid solutions.

The vessel was emptied through tap 5 by opening tap 9 to atmosphere and the potentiometric titration of the iodine carried out under nitrogen.

Collection and processing of the blank.

The reagents in the capillary limbs were run into the reaction vessel as they were possibly contaminated, and excess of the acid reagent was always added. Nitrogen pressure was then increased in the reaction vessel and forced the reagents back into the reagent tubes. During the blank determination no special precautions were taken to exclude air as both water and reagents were pure.

After the small quantities of reagent in the reaction vessel had been flushed out three times, 500 ml. of deaerated water at 20°C. were transferred to the reaction vessel. The reagents were run in in the order alkaline iodide/iodine, acid and manganese solutions.

The iodine was titrated as before.

Air-Saturated Water.

The oxygen dissolved in the air-saturated water was estimated by the "reversed-reagents" method. The free iodine concentration in the alkaline reagent was increased to obtain a blue starch complex colour in the blank titration.

The reagents were added by 1 ml. pipettes whilst the flasks were submerged in the gas jars and after each addition the flasks were stoppered, taken out, and shaken. 100 ml. of the solutions were titrated with 0·1N sodium thiosulphate using a starch

indicator. The inherent errors were calculated and found to give rise to an insignificant error in the estimation of the diluted sample.

9:4. MODIFICATION OF STANDARD PROCEDURE.

Acid reagent.

In the early experiments on the apparatus it was noticed that occasionally a visible brown colouration appeared in the solutions on addition of acid reagent. This was recognised as iodine, presumably released from the potassium iodide by local heat generation resulting from the neutralisation of the hydroxide. Even when the acid was run in very slowly this still took place at times. This was overcome by diluting the A.S.T.M. recommended concentrations1:4 with water. The results reported were obtained with the diluted reagents.

Sodium thiosulphate.

It was found that in the range 0·012 - 0·060 p.p.m. of dissolved oxygen, 0·005$\bar{N}$ sodium thiosulphate was suitable for titrating the iodine, but for the lower oxygen concentrations 0·002$\bar{N}$ solutions were better

9:5. Poisoning of Platinum Electrode.

Another source of error appeared at regular intervals. It was characterised by a gradual decrease in the accuracy of the results. This error gradually increased until after about thirty titres it approached 0·006 p.p.m. After this had taken place a few times it was possible to attribute it to poisoning of the platinum electrodes as correct results were obtained as soon as a fresh foil electrode was used.

With experience it became possible to detect the onset of this poisoning by observing the potential behaviour after an increment just before the end-point.

The potential is taken every few seconds for two or three minutes. Normally, this drops rapidly, reaching a steady value, then rises very slowly. However, a rapid decrease followed by a rapid rise indicate that the electrode is poisoned.

The causes of this behaviour have not yet been proved. It had been noticed that the abnormal behaviour was marked when the titration had brought the potential to a value between 0·35 and 0·31 volts, the approximate end-point. In fact the rapid rise in potential characteristic of a poisoned electrode tended to bring the potential back to about 0·35 volts. After the end-point was passed the behaviour of a poisoned electrode was similar to a normal one.

The form of electrode and method of storage were altered to find out if these were critical factors. Short and long platinum wires, large and small foil electrodes all became poisoned. Electrodes were stored in air, demineralised water, dilute HCl. concentrated HCl, dilute HNO_3, 10$\bar{N}$ HNO_3, and concentrated HNO_3. One electrode was dipped in concentrated HCl and heated to red heat before each titration. Each of the changes failed to delay the onset of abnormal behaviour. Cleaning with organic solvents also failed to effect any improvement.

The only clue to the nature of this poisoning came when a poisoned electrode was being cleaned by electrolytic evolution of gas from its surface. It was observed that the current passing, and hence the evolution of gas, was greatly increased when the electrode was taken out and cleaned with emery paper. This suggests that the interference is due to a surface film of contaminant.

Young (21) is the only author found in this field mentioning a similar phenomenon. He ascribes it to contamination by sulphur produced by the decomposition of the acidic thiosulphate during the titration. However this may not be the sole reason as it can be deduced from a study of his work that his electrodes showed poisoning even when iodine estimations were carried out with thiosulphate. Young continually replated his platinum electrodes by putting them in a platinum electroplating solution between tests. Other explanations for this phenomena could be contamination by mercury from the calomel electrode or from the silicone grease used as a stopcock lubricant. During the present work the platinum foil electrodes were stored, in 10$\bar{N}$ nitric acid, as recommended by Kolthff (55), and replaced when they showed abnormal tendencies.

The author feels that the poisoning is due to the silicone grease.

9:6. RESULTS AND DISCUSSION.

The results obtained for the estimations of oxygen dissolved in pure water are shown in table 5.

These results show that the mean of the difference between the oxygen added and the oxygen measured is nil and the standard deviation of these differences is 0·0018 p.p.m. The A.S.T.M. (80) define "accuracy" as the algebraic difference of the average result of a series of controlled determinations from the true value, and "precision" as the standard deviation of the results. Therefore the results compare favourably with the values given for the A.S.T.M. test for dissolved oxygen.

	Accuracy	Precision
A.S.T.M. specification	0·003 p.p.m.	0·002 p.p.m.
Present work	0	0.0018 p.p.m.

Although the test results show no bias it is probable that the residual oxygen in the "oxygen-free" water is similar to the value of 0·0006 p.p.m. obtained by Potter (6). This value could be ascertained by making numerous measurements at "zero oxygen" content.

In the apparatus described, freeing the reagents of dissolved oxygen dispenses with the need to use the correction of 0·010 p.p.m. given in the A.S.T.M. method. This correction for oxygen dissolved in the reagents should obviously be avoided if possible, as it is affected by changes in temperature and pressure. Also, in some cases, it becomes necessary to make a correction which is greater than the net quantity being estimated. The apparatus was deemed successful, and the results showed that no error was introduced by the deviation from the normal practice of preparing a sample and blank simultaneously.

The fact that air-saturated water was not added to the blank did not affect the results. This was to be expected as only pure water was used and the blank is not affected by oxygen but only by interfering substances. Also, of course, the method of collecting the blank results in a high oxygen content and the addition of the small amount of oxygen added to the sample would have little effect.

CHAPTER 10.

THE ESTIMATION OF MICRO QUANTITIES OF OXYGEN IN WATER CONTAINING HYDRAZINE.

10:1. INTRODUCTION.

It was assumed until recently that the A.S.T.M. oxygen-analysis (7), developed from the Schwartz and Gurney "reversed-reagents" technique (11), overcame interference caused by reducing agents. The appropriate literature has been reviewed in Chapter 4 and the review is extended here to include observations relevant to the problem of hydrazine interference.

Janssen (81), using a Winkler method, attributed interference in the presence of sulphite to a reaction between sulphite and dissolved oxygen. Potter and White (43) found that a "reversed-reagents" oxygen analysis gave erroneous results when Fe^{++} was present. Other authors (10), (22), (39), (40), (41) have reported a similar effect. Potter and White's explanation of the "uncorrected-interference" is given in Chapter 4. Sebald (13), however, found no "uncorrected-interference" from ferrous ions.

A similar confusion exists in the literature on the estimation of dissolved oxygen in the presence of hydrazine. Some authors (89) have estimated oxygen in the presence of hydrazine by employing "reversed-reagents" techniques others have had to devise special procedures. Wickert and Ipach (39) removed the hydrazine by oxidation with bromine water (the excess bromine being neutralised with sulphosalicylic acid) and then proceeded with a Winkler-type estimation of oxygen. Potter and Everitt (90) found that interference was avoided when the hydrazine was removed with an "equilibrated" cation-exchange resin placed before the sample vessels. Freier (16) has commented unfavourably on the use of the o - tolidine method when hydrazine is present. Freier, however, treated the "blank" of the "reversed-reagents" analysis by adding acid first. Potter (6) points out that this complete reversal of the order of reagent addition to the "blank" compared with that for the "sample" does not correct for substances which react preferably in alkaline solutions.

One unambiguous method of testing the effect hydrazine has on a dissolved-oxygen analysis is to obtain a sample of oxygen-free water and add known quantities of oxygen then oxygen-free hydrazine to it. If a "reversed-reagents" oxygen-analysis is then performed on this sample and "oxygen-free" reagents are employed the result should be equal to the oxygen added. Using this procedure oxidation of hydrazine in the feed-line, catalysed by impurities or surface effects, is avoided. The results obtained for the oxidation of

hydrazine in aqueous solutions (91) indicate that this autoxidation would be negligible in the time required for an analysis. The results from the analysis procedure proposed above should indicate whether or not hydrazine itself or hydrazine plus the impurities present in the "Analar" reagents can affect a "reversed-reagents" analysis of dissolved oxygen.

10:2. EFFECT OF HYDRAZINE ON ESTIMATIONS.

In the present experiments the hydrazine reagent was freshly prepared from solid hydrazine sulphate (A.R.) before each estimation. The concentration was adjusted to give 0.020 p.p.m. of hydrazine in the reaction vessel.

The estimations were originally made as detailed in Chapter 9 and the reagents were added in the order shown overleaf.

	SAMPLE	BLANK
1.	Air-saturated water	-
2.	N_2H_4	N_2H_4
3.	$KOH/KI/I_2$	$KOH/KI/I_2$
4.	$Mn\ SO_4$	H_2SO_4
5.	H_2SO_4	$Mn\ SO_4$

It was observed that the results obtained were consistently low. This was attributed to the fact that the sample and blank were not processed under the same conditions and contained different concentrations of oxygen. In the results quoted for pure water this factor was not critical.

Before modifying the procedure tests were carried out to discover whether there was any variation in the results with differing times of contact between dissolved oxygen, hydrazine and alkaline solution. The air-saturated water was added to the sample followed immediately by the hydrazine, the solution stirred for 15 seconds and the alkaline reagent added. The time between the alkaline addition and the manganous solution addition was varied and the results are shown in table 6.

During the tests quoted in table 6 periodic checks were carried out to ascertain that the apparatus was still producing accurate results in the absence of hydrazine. Three of these tests are shown in table 7 when this check was carried out immediately before or after one of these estimations in table 6 had been made, and hence the free iodine concentrations added with the alkaline reagents are likely to be similar in the sample and blank of each pair.

The results in tables 6 and 7 are discussed in section 10:4.

Several modifications of the procedure used for the estimations of the blank were made and although successive modifications reduced the discrepancy, only the procedure described below gave acceptable results.

10:3. MODIFIED BLANK PROCEDURE.

The technique of preparing the blank had to be altered so that it could be processed under "oxygen-free" conditions. The sample technique remained as described in the experiments on pure water.

After the sample had been run from the reaction vessel the situation is that

this vessel is full of air and the reagents in the capillary limbs are probably air-contaminated, but the remainder of the apparatus is under a nitrogen atmosphere.

Taps 4, 5, 6 and 7 in fig. 19 were closed and the reaction vessel was thrice evacuated and filled with nitrogen. Whenever possible nitrogen was passed through the 2 litre flask. When this could not be done tap 2 was closed to prevent contamination by water sucking back from the trap as the deaerated water cooled. When the reaction vessel was finally filled with nitrogen, some of the reagents were displaced by nitrogen into the vessel to flush out the capillary connections. The limb connecting tap 6 to the reaction vessel was flushed out with air-saturated water and enough acid run into the reaction vessel to acidify the waste reagents.

These waste reagents were displaced through tap 5. During this operation taps 9 and 2 were adjusted to keep nitrogen flowing through them until the reaction vessel was empty. After a small volume of acid reagent had been run into the reaction vessel the reagents, in turn, were slowly blown back by nitrogen into their respective side necks and the last traces of reagents in the reaction vessel washed out three times by deaerated water as described previously. The acid reagent neutralised any alkali on the sides of the reaction vessel.

500 ml. of deaerated water were transferred to the reaction vessel in the manner described for the sample in section 9:3. The appropriate amount of air-saturated water was injected immediately followed by hydrazine. Fifteen seconds later the alkaline/iodide/iodine was added, the solution stirred for 3 minutes, then sulphuric acid slowly run in, and manganous solution introduced after a further 3 minutes had elapsed. This modified blank procedure enabled the results in table 8 to be obtained.

10:4. DISCUSSION OF RESULTS OBTAINED IN THE PRESENCE OF HYDRAZINE.

The results obtained in table 6 consistently underestimate the oxygen present. The variation of contact time with the alkaline reagent does not appear to have a significant effect and the interfering reaction therefore appears to take place in less than $1\frac{1}{2}$ minutes. The investigation was not carried on with contact times less than $1\frac{1}{2}$ minutes as conflicting results could then arise due to differences in stirring. Instead the work was concentrated on the modified blank procedure as this showed signs of producing correct results.

The mean of the differences between the oxygen added and the oxygen measured

in Table 8 is nil and the standard deviation of these differences is 0·0022 p.p.m. That those results are within the A.S.T.M. specification is shown below.

	Accuracy (p.p.m.)	Precision (p.p.m.)
A.S .T.M. specification	0·003	0·002
Results with pure water (Table 5)	0	0·0018
Results of Table 8	0	0·0022

The "differences" in Table 6 have a negative bias of -0·008 p.p.m. and a standard deviation in the order of 0·002 p.p.m. This negative bias contrasts sharply with the non-biased results for Table 8. The significance of Table 7 is that the "sample" titre is decreased in the presence of hydrazine whilst the "blank" remains virtually unchanged. This is expanded in Chapter 12.

The contrast between Tables 6 and 8 could not be investigated further as the stopcocks on the apparatus had deteriorated to such an extent that the apparatus was considered unusable. High-vacuum taps from all recognised British manufacturers had been used and none gave continuous satisfaction. The effects of deterioration are noted in Section 11:1.

Since the apparatus had become unreliable no further conclusions were drawn from this work. A report of further experiments employing a different apparatus is given in Chapter 12. The work leading to an explanation of the role of hydrazine in the "reversed-reagents" analysis of dissolved oxygen is given in Chapter 12 and in the Section 12:4 certain comments are made regarding Tables 6 and 8.

CHAPTER 11.

THE ESTIMATION OF DISSOLVED OXYGEN IN THE RANGE 0-0·020 p.p.m. UTILISING A MODIFIED SAMPLING TUBE.

11:1. INTRODUCTION.

During the experiments quoted in Chapter 10 the performance of the high-vacuum stopcocks in the apparatus deteriorated. This deterioration was exhibited during the evacuations by the tendency to draw up water from the gas traps. Latterly after each estimation every tap had to be cleaned and regreased before a satisfactory vacuum was maintained. The deterioration in the taps had the additional effect of drawing grease into the reagent tubes which resulted in the reagent columns breaking up when the nitrogen bubbles passed through. When this happened that estimation had to be abandoned as it was impossible to add replicate volumes of reagents to the "samples" and "blanks". The ratio of completed tests to abandoned tests eventually became such that a new apparatus was designed to continue the work on hydrazine.

The circumstances that had dictated the choice of the apparatus of Chapters 9-10 were no longer applicable as a feed-water treatment plant with a 50 lr/hr. output of deaerated water was, by then, available. This plant is associated with an experimental supercritical steam generator constructed by the Department. In these circumstances a sampling tube of a flow-through type was deemed desirable.

According to the literature the two sampling vessels which have given most satisfactory performance are those used by Potter (fig.12c) and Young (fig.13). It was decided to base the new tubes on Potter's sampling tubes.

11:2. SAMPLING TUBES.

The 500 ml. sampling tubes (fig.21) were manufactured from "Pyrex" glass and fitted with "high-vacuum" type stopcocks. The "V-bore" tap at the top of the sample tubes was preferred to Potter's arrangement as it was considered that this tap, which is widely manufactured, would prove less dependent on specialised glass blowing. The taps in the sampling tubes were reground after the whole apparatus was annealed.

It was intended to sample cooled deaerated water and attempt to lubricate the taps with water only. If this failed, and silicone grease had to be applied, then, as the tubes were to be used at atmospheric pressure, it was expected that the taps would give better performance than in the previous

apparatus. It was also possible that, even using grease, this system would give an improvement in the electrode behaviour as no grease would be drawn into the tubes by evacuation. It transpired that electrode contamination recurred.

The sample tube had a flat base to allow stirring during the estimation. The stirrer armature was slipped through the 4 mm. tap then the glass bend was butted and attached to the sample tube with thin p.v.c. tubing. Unless noted otherwise this procedure was adopted for all glass/glass connections. Stirring during reagent additions would minimise the errors due to the sinking of the dense reagents and their subsequent ejection through the bottom tap (Potter ref. 6,p. 298). The high vacuum taps were fitted to avoid ingress of air either due to the stirring vortex causing a partial vacuum inside the tubes or from contraction of the sample.

The actual injection of reagents must be considered when accurate dissolved-oxygen measurements are attempted. Potter's sampling tube has a volume of 250 ml. and a permanent capillary reagent-tube calibrated to deliver 0·125 ml. The design of the sample tube (fig. 21) was such that provision was made to allow either a calibrated capillary or another type of tube to be attached.

There are three approaches to the question of reagent addition. The reagents may be deaerated, a constant correction may be made, or a small volume of air-saturated reagents can be injected. The 2 ml. increments of the A.S.T.M. test give, for a 500 ml. sample, a constant correction of 0·0104 p.p.m. with a variable error due to atmospheric temperature and pressure changes. This variable error leads to a degree of uncertainty and for primary calibration it is preferable either to add volumes less than 0·02 ml. without deaeration or to deaerate and have an injection procedure whereby air contamination is avoided.

Some preliminary tests were carried out to determine the difficulties in adding reagent volumes less than 0·1 ml. A capillary tube was marked as in fig. 12(c) so that the volume between the end of the tube and the calibration mark was 0·02 ml. This capillary was attached to the sampling tube in the position shown for the burette tubing in fig. 21. It was soon evident that either the contraction or expansion of a 500 ml. sample volume or the hasty manipulation of the two stopcocks could cause considerable percentage differences in successive additions. This was also found to a lesser degree when 0·05 ml. additions were attempted. If reagent additions of less than

0·1 ml. were made during an A.S.T.M oxygen-analysis it would often be obligitary to add relatively high concentrations of free oxidant (iodine) to the alkaline reagent. This would necessitate accurate duplication of the alkaline reagent added to the "sample" and "blank" and the preliminary tests showed that this could not be achieved consistently. Although Potter has produced highly satisfactory results with a 0·1 ml. addition it was considered that, as this addition volume would require reagent deaeration (or a constant correction of 00005 p.p.m.) and would still involve considerable care in manipulation, the arrangement shown in fig. 21 would give similar results and permit a certain laxity in reagent addition.

With the arrangement shown in fig. 21, 0·5 ml. additions can be made with no manipulative difficulties. Another factor in favour of the final arrangement is that it can also be used to add air-saturated water for calibration purposes and is more versatile than the fixed one-mark tube i.e. the effect of different reagent volumes can be assessed.

0·5 ml. reagent additions and a 500 ml. sample were chosen for various reasons. If the reagents have a residual oxygen content which would introduce a constant error then the larger the sample the smaller is the percentage of this error. If only a small excess of oxidant is added to the alkaline reagent then, with the volumes quoted, small differences in volumes of reagents added to the samples are relatively unimportant. Potter's results show that 0·1 ml. increments of A.S.T.M. reagents are sufficient to enable the Winkler reactions to go to completion when low oxygen ranges are being analysed, therefore 0·5 ml. of reagents 1/5th. of this concentration could be expected to produce the same effect.

11:3. FEED-WATER TREATMENT.

A flow chart of the treatment plant is shown in fig.(22). Three materials were employed in the pipelines. The tubes from the main's water to the resins were of "alkathene", those from the resins to the deaerator were of glass and p.v.c., and those from the deaerator onwards were of glass (butted and joined with p.v.c.). The pressure filter was a small "Metafilter" unit, the constant-head tank was of stainless steel, the resins were contained in " Perspex" tubes. The cooler was a 13-coil "Pyrex" heat exchanger, and the analyser was a Cambridge "gas-transfer" electrochemical analyser.

In the present work the treatment plant was operated with a flow of 30 litres per hour; the filter material changed every 10 hours; and the

first mixed-bed resin regenerated whenever the conductivity of the water flowing from it rose to $0{\cdot}2 \times 10^{-6}$ ohm^{-1} $cm.^{-1}$ A system of three mixed-bed resins was utilised which allowed two to be on service in series whilst the third was being regenerated. The freshly-regenerated bed was put into service as the second bed in the series. This arrangement ensured that when the first bed was becoming exhausted, water of a uniform high quality still entered the deaerator.

Preliminary tests showed that the resins lost capacity between successive regenerations and eventually an unusually slow rise in the conductivity was obtained when a bed was becoming exhausted. These are typical signs of contamination caused by organic acids (humic and fulvic) in the water supply (92) and this was confirmed by chemical analysis (not by author). Contamination was avoided by periodically rinsing the resins with a sodium chloride/sodium hydroxide mixture (92). There was an expected decrease in capacity of the resins following each chloride/hydroxide rinse but the capacity remained constant between rinses.

The quoted conductivity shows that the water used in the experiments contained little ionised impurities. Tests on the freezing-point depression carried out in the Department, not by the author, showed that the organic matter in the water was non-detectable. This was done by measuring the temperature of the "triple point" of water in a standard "triple-point cell". These results were:-

(1) International Standard for temperature of the triple point of water = $0{\cdot}0100^{\circ}C$.

(2) Temperature of triple point of water with a cell prepared according to National Physical Laboratory specification (93) :-

Departmental measurement = $0{\cdot}0097^{\circ}C \pm 0{\cdot}0005^{\circ}C$

N.P.L. measurement = $0{\cdot}0097^{\circ}C. \pm 0{\cdot}0001^{\circ}C$

(3) Temp. of triple point of water using deionised water from water-treatment plant.

Departmental measurement = $0{\cdot}0100^{\circ}C \pm 0{\cdot}0005^{\circ}C$.

The uncertainty in the Departmental measurements is equivalent to 0·0002 moles/litre of organic matter. The subsequent dissolved-oxygen estimations showed that even if this quantity was present it did not interfere with the measurements.

The glass deaerator was constructed from glassware fitted with

standard joints. It consisted of three main parts - a 10 litre boiling-flask, a stripping column packed with stainless-steel Lessing rings and a heat exchanger which heated the feed-water and cooled the flow from the deaerator.

The glass bends on the sampling tubes (fig.21) were connected to the feed-line (fig.22) by 2" lengths of neoprene tubing ($\frac{1}{4}$ inch wall thickness). It would appear that no appreciable ingress of oxygen results from use of neoprene of these dimensions (72), (94).

11:4. "DEAERATION" OF REAGENTS.

It has been reported (46) that nitrogen passing through a 0·1 molar potassium chloride solution for 30 minutes reduces the dissolved oxygen content by 98%. One could reasonably expect that when air-saturated water is treated thus, 1 ml. of the treated water when added to a 500 ml. sample of test water would raise the oxygen level of the latter by about 0·0002 p.p.m. As the Winkler reagents contain less oxygen than air-saturated water and it was intended to "deaerate" for a longer period than 30 minutes, then 0·5 ml. additions of each reagent, deaerated thus, should introduce a small constant error to an A.S.T.M. "reversed-reagents" analysis. It was expected that the maximum order of this error would be about 0·0001 p.p.m. i.e. the lower limits of the analysis.

The oxygen content of the reagents was reduced in the flasks shown in fig.23. The deaeration line was essentially a glass manifold to which duplicated sets of reagent flasks were fitted and one set of reagents was used for each pair of sampling vessels. "Oxygen-free" nitrogen (10 volumes oxygen/million volumes of nitrogen) was passed through the reagents for at least 2 hours before they were used.

11:5. REAGENTS.

The reagents were prepared from "Analar" grade chemicals and water which had been distilled and passed through a mixed-bed resin of "Analar" grade. As a result of the experience gained in the work described in section 9:4 the reagent concentrations were maintained at one fifth of the concentration recommended for the A.S.T.M. "reversed-reagents" analysis (7).

11:6. SAMPLING.

The sample tubes were taken from the feed line, for an oxygen analysis, after deaerated water had been passing through them for a minimum of 2 hours. This was found to give a correct sample and the analyser was by that time recording a steady maximum value (Table 12). The relatively slow equilibration

of the model used did not prove a disadvantage as the oxygen level of the deaerated water on each day's run seldom varied by more than 0·0002 p.p.m. The oxygen content of the deaerated water actually varied from 0·001 - 0·003 p.p.m., depending on the time the deaerator had been idle or the period of continuous use.

When a pair of sampling tubes was removed from the line, one of the calibrated overflows (fig.22) was opened to keep the flow from the deaerator constant. This stabilised the operating conditions of the deaerator.

11:7. OXYGEN ANALYSIS.

The tubes containing the sample were taken from the line and placed on magnetic stirrers. The reagent flasks were then detached in turn from the reagent-deaeration line and connected by the p.v.c. tubing (fig.23) to the burette tubing on the sample tubes. The reagent was blown into the burette tubing and out to waste until all the entrapped air was swept out. The "V" bore tap was then turned to leave the burette tubing filled with the reagent solution. After removing the reagent flask the reagent solution was first run down to the zero mark on the burette tubing and then 0·5 ml. was slowly introduced into the sample tube.

It has been found that stirring during the reagent injections did not contaminate the sample with air and prevented the denser reagents passing through the solution and being ejected from the bottom tap. After each reagent addition the burette tubing and waste outlet were washed with distilled water, dilute sulphuric acid, and again with distilled water.

The dimensions of the neck below the "V" bore tap were such that two conditions favourable to accurate analysis were obtained. The manganese hydroxide precipitate was kept suspended throughout the whole tube without resorting to violent stirring and thus it reacted uniformly with all the oxygen present. Also, when the acid reagent was run in, a representative sample of the oxidised hydroxide was ejected through the bottom tap.

When a sample had been processed it was run into the titration beaker via a length of glass tubing which was temporarily attached to the glass bend of the sample tube. The bottom of this tube was kept above the gradually rising level of the transferred sample thus reducing aerial mixing. Potter and White (43) filled the titration vessel with nitrogen and kept nitrogen sweeping over the electrodes during titrations. In the present work the end-point response was so positive that the nitrogen bubbler was used solely to

obtain vertical mixing. Although iodine was seen to be released when a sample was left overnight in the titration vessel, the results show that either this aerial oxidation of the iodide was negligible or was constant in the "sample" and "blank" and thereby cancelled in the final result (the time taken to titrate a "sample" or "blank" being approximately similar). Therefore the only precautions taken were to minimise aerial mixing during the transfer to the titration beaker.

When tests were made at oxygen levels higher than that of the deaerator flow the appropriate volume of air-saturated water was injected into the samples. The air-saturated water was run from a 15 litre bottle through the 1 mm. bore waste-exit of the sampling tubes to flush and fill the burette tubing. At the same time it was run into two standard flasks to give samples which were used for a "submerged-bottle" oxygen analysis of the air-saturated water (see Section 9:3). 0·02 $\bar{N}$ thiosulphate was employed to titrate the iodine released in the analysis of the air-saturated water (starch indicator).

11:8. ELECTROCHEMICAL END-POINT DETERMINATIONS.

Initially the iodine released by the "Winkler" reactions in the sample tubes was estimated potentiometrically using a platinum/calomel electrode pair and a vernier potentiometer with a galvanometer photocell-amplifier unit attached. The electrode fouling previously experienced recurred. As the present experiments were intended to achieve a higher accuracy than that obtained with the previous apparatus it was found necessary to make a new platinum electrode each day.

It was therefore decided to adopt the "dead-stop" end-point technique (95) which has been refined for this application by Potter and White (6) and Bishop (96), (97). The development of this method is described in Chapter 13. It can be said here that the fouling was overcome and adequate sensitivity and consistency were obtained.

0·002 $\bar{N}$ and 0·001 $\bar{N}$ thiosulphate (A.R.) were used for titrations with the potentiometric and "dead-stop" end-points respectively.

11:9. EXPERIMENTAL TECHNIQUES AND RESULTS.

The dissolved oxygen content of the water from the deaerator was estimated by chemical analysis and in Table 13 these results are compared with the readings shown on the Cambridge meter. Four of these results were taken with air-saturated water added to the flasks (the meter being used to determine the base oxygen level i.e. the oxygen in the deaerator output).

A correction applied to these four results is discussed in Section 11:10.

The order of reagent addition for Table 13 was:-

"Sample" - column A - (a) Potassium hydroxide/iodide/iodine. (b) Manganous sulphate. (c) Sulphuric acid.

"Blank" - column B - (a) Potassium hydroxide/iodide/iodine. (b) Sulphuric acid. (c) Manganous sulphate.

A statistical treatment of column G in Table 13 shows that the standard deviation (precision) of the differences between the physical and chemical measurements is 0.0008 p.p.m. and the mean value of these differences is practically zero. These results showed that the new apparatus was satisfactory when compared with the meter.

Tests on the recovery of added oxygen were carried out to investigate whether the precision of 0.0008 p.p.m. was a function of the chemical analysis or was due to the analyser. In these tests (Table 14) the appropriate volume of air-saturated water was added to one of a pair of samples and then the A.S.T.M. "sample" procedure was applied to both. The meter was used to record the oxygen content of the deaerator output and the results in Table 13 show that this could be done with confidence. The order of reagent addition for Table 14 was:-

Sample 1 (column A) - (a) Air-saturated water (if added). (b) Potassium hydroxide/iodide/iodine. (c) Manganous sulphate. (d) Sulphuric acid.

Sample 2 (column B) - (a) Potassium hydroxide/iodide/iodine. (b) Manganous sulphate. (c) Sulphuric acid.

Table 15 shows that a statistical treatment of Table 14 results in an accuracy of -0.0005 p.p.m. and a precision of 0.0007 p.p.m. for the results in Table 14.

There was a time lag and a mixing of reagent solutions between the addition of one reagent to "Sample 1" and its addition to "Sample 2". The negative bias of the differences in Table 14 is taken to show that an oxygen pick-up occurred. It should be noted that this systematic error would not normally occur in a dissolved oxygen analysis as the oxygen in the "blank" does not affect the results when pure water is being tested. This negative bias bears comparison with that obtained by Potter and White who used a more refined method of reducing the oxygen content of the reagents. This comparison is discussed in Section 11:11.

11:10. CORRECTION FOR THE ERRORS IN "AIR-SATURATED WATER" ESTIMATION.

When the dissolved oxygen in the air-saturated water is estimated by the "submerged-bottle" technique several errors can arise. That due to the oxygen in the reagents was previously ignored (Chapter 9) but in the present work the desired accuracy was higher and it was either necessary to measure the oxygen in the reagents or, following Potter and White, deaerate these reagents. It was decided to measure the oxygen in the reagents and, using this as a constant correction, allow the small daily variation due to temperature to appear in the overall precision of the tests. This could be done as the volumes and concentrations of the reagents were such that the constant correction for an oxygen analysis, performed in 500 ml. samples at oxygen levels below 0.02 p.p.m., was equivalent to less than 0.0001(5) p.p.m. The variance in the correction factor was not then significant even though the desired overall accuracy was high.

Table 16 shows the estimation of the total oxygen content of 1 ml. of the alkaline/iodine solutions and 1 ml. of the manganous solutions which were used to estimate the oxygen content of the air-saturated water. The order of reagent addition was as described in Section 11:9 for the "samples" and "blanks" of Table 13. In this case however 0.6 ml. of each reagent (air-saturated) was added and the results were calculated to give the total oxygen content of the 1 ml. of each of the reagents added during the analysis of the air-saturated water. The mean value of 0.0124 mg. was used in the correction factor.

The full correction was:-

$$A = \frac{B}{C}\left[(C-2).F+G\right]$$

Where A = Iodine titrated expressed as mg. of oxygen.
B = Volume titrated (ml.).
C = Total volume of air-saturated water sample (ml.).
G = mg. of oxygen contained in the added solutions of alkaline/iodide/iodine and manganous sulphate.
F = Corrected value of the dissolved oxygen value of the air-saturated water (mg./ml.).

The assumptions on which this correction was based were:-

(a) When the acid was added to the sample all oxidised manganese was contained in the settled precipitate.

(b) As the final result was based on a subtraction of two titres, the sensibly constant starch-indicator uncertainties cancel.

(c) Similarly the errors caused by displacement of free iodine cancel.

When the oxygen in the air-saturated water was estimated the free iodine in the reagents was minimised and the depth of immersion of the tops of the sampling flasks was reasonably small and sensibly constant.

11:11. DISCUSSION OF RESULTS.

Table 15 shows the present results compared with those of Potter and White. It is seen that the precision of analysis of "recovery of dissolved oxygen" is similar but a more negative bias appears in the present results (the terms "precision" and "accuracy" are used in accordance with the A.S.T.M. definitions - ref. 80). The slightly greatly negative bias is therefore attributed to the simpler general technique used in the present work and it is considered that the accuracy is still acceptable. The fact that the results obtained from the comparison with the Cambridge analyser are also acceptable is taken to justify the use of the analyser to obtain the values of the oxygen level in the feed-water in Tables 14 and 16.

CHAPTER 12.

THE ESTIMATION OF MICRO QUANTITIES OF OXYGEN IN WATER CONTAINING HYDRAZINE.

12:1. INTRODUCTION.

The estimation of dissolved oxygen in the presence of hydrazine has been described in Chapter 10. However, the apparatus had deteriorated when these results were taken and this, allied to the paucity of actual results, made the validity of the results uncertain. The apparatus and techniques described in Chapter 11 were used to check and extend the work reported in Chapter 10.

The results in Chapter 10 indicated that a comparison between pairs of "samples" and "blanks" in which hydrazine was present and those in which it is absent might show the nature of the interference. This comparison was carried out with the new apparatus described in Chapter 11.

12:2. REAGENTS AND TECHNIQUES.

The reagents for the A.S.T.M. type analysis were prepared and deaerated as described in Chapter 11. "Analar" reagents were used as the results would indicate if it would be necessary to purify them further. The hydrazine solutions were prepared from known weights of "Analar" hydrazine sulphate and deaerated before use (along with the A.S.T.M. reagents) in the apparatus shown in fig.23. The hydrazine concentration was estimated (Chapter 14) by volumetric analysis and resulted in a value less than 0.001 p.p.m. smaller than the concentration according to weight.

The feed-water sampling techniques, addition of reagents, and deaeration of reagents were as detailed in Chapter 11.

12:3. EXPERIMENTAL RESULTS.

Table 17 shows the results for the analysis of oxygen in the presence of hydrazine. The order of reagent additions used for these experiments was:-

"Sample". - (1) Air-saturated water(if added). (2) Hydrazine. (3) Potassium hydroxide/iodide/iodine. (4) Manganous sulphate. (5) Sulphuric acid.

"Blank". - (1) Air-saturated water (if added to "Sample"). (2) Hydrazine. (3) Potassium hydroxide/iodide/iodine. (4) Sulphuric acid. (5) Manganous sulphate.

The electrochemical analyser was used to obtain the oxygen level of the feed-water i.e. the deaerator output (column D, Table 17).

Table 17 showed that oxygen estimations in the presence of hydrazine were consistently low and that this error increased with increasing oxygen values. The error appears slightly larger than that reported by Potter and his

colleagues (ref.83; pp.53 and 138), (90) who obtained an error of -0.005 p.p.m. when 0.015 p.p.m. oxygen was estimated with 0.02 p.p.m. hydrazine present. However both observations result in the same conclusion that there is "uncorrected interference".

Rees and Taylor (98) give 0.007 p.p.m. as the maximum oxygen value tolerated in C.E.G.B. power stations and Table 17 therefore indicates possible causes of the contradictory literature reports mentioned in Chapter 10. Firstly, as hydrazine makes no difference to the mechanics of an A.S.T.M. type oxygen-analysis, then, if the true oxygen value is unknown, "results", which are incorrect, may be reported in good faith. Secondly, at oxygen levels below 0.008 p.p.m. and with 0.02 p.p.m. hydrazine present (according to Potter, ref.85 p.53, "a value relevant to boiler practice") estimations may be obtained which are just within the limits given for the A.S.T.M. test (7) i.e. accuracy = 0.003 p.p.m. and precision = 0.002 p.p.m. Therefore contradictory reports as to hydrazine interference may be due to a failure to define the accuracy of an analysis or the use of an ambiguous technique.

There are many different possibilities for the mode of behaviour of hydrazine during a "reversed-reagents" analysis of dissolved oxygen. For the purposes of a uniform terminology it is intended to use the word "reaction" for the various modes of behaviour discussed in this section even though the list shown below contains a possibility of no reaction. The term "oxidant" refers to the free iodine added initially to the alkaline reagent.

Some of the possible "reactions" are:-

(a) Total oxidation of hydrazine by the oxidant.

(b) Simultaneous oxidation of the hydrazine by the oxidant and dissolved oxygen in alkaline solutions (the hydrazine being completely oxidised).

(c) No reaction of hydrazine throughout the analysis.

(d) Differences in the degree of hydrazine oxidation in "samples" compared to that in "blanks".

(e) Differences in the oxidation of hydrazine at increasing oxygen concentrations due to catalysis by metal ions introduced with the reagents e.g. manganese, present in the "Winkler" reagents, or iron and copper present as impurities in the "Analar" reagents.

It appears that reactions (a) or (c) do not take place as there would then be no "uncorrected interference" as found both by Potter and in the results shown in Table 17.

Some of the other possible modes of hydrazine reaction can be eliminated by studying the results from suitable reaction sequences. Differing reaction sequences were used and the results appear in Tables 18A - 18E.

The headings of these various sub-tables show the order of reagent additions to the samples. The horizontal lines of results, within each sub-table were obtained from samples taken at the same time and these samples were processed with reagents from the same "deaeration" flasks. In Tables 18A - 18E no estimation of the oxygen content of the added air-saturated water was made as, at that stage, only qualitative results were sought. Therefore, when 0.6 ml. of air-saturated water is shown to have been added, it can be assumed that the final oxygen level of the solution was approximately 0.012 - 0.015 p.p.m., and each of the samples being compared had equal oxygen values. The reagents used in this series of tests were "deaerated" before use.

The reaction between hydrazine and dissolved oxygen is more pronounced in alkaline than acid solution (ref.82, p.139), (91). If reaction (b) took place, more hydrazine would react with dissolved oxygen in the alkaline solutions leaving more free oxidant present in these solutions. This would be shown by the first set of results in Tables 18A and 18B being greater than those from the second reaction sequence. This did not happen and it is therefore probable that the "uncorrected interference", found when hydrazine is present, is not due to some form of reaction (b), as the Tables show that there is no difference in the reactions in alkaline or in acid solutions.

Table 18C shows that, within the precision limits of the method, the added oxidant was not oxidising the hydrazine. This must be stated with the proviso that the results discussed above excluded the possibility of a hydrazine/oxygen reaction in alkaline solutions. Tables 18D and 18E indicate that hydrazine produced an effect in the "sample" of a "reversed-reagents" analysis which was not duplicated in the "blank". Reaction (d) is therefore possible i.e. there is an oxidation of hydrazine in the "sample" and not in the "blank".

At this stage it was difficult to assess whether the "uncorrected interference" was solely due to adventitious ions. It can be noted however that hydrazine had little effect on the "blanks" at varying oxygen levels. If reaction (e) took place to an appreciable extent then, depending on the oxygen

level, some of the results with hydrazine present should differ from those obtained in its absence. This question is dealt with later in this Chapter.

The work just described seemed to indicate that there was no appreciable oxidation of hydrazine in the reversed-reagents "blanks" at the concentrations quoted, but that there was an oxidation in the "samples". It is probable that this oxidation resulted from the oxidised manganese present in the "sample", as this was the only change in reaction species which could account for it.

Potter has published about 10 results which indicate that the magnitude of the "uncorrected interference" increases as the hydrazine and oxygen levels increase. The qualitative experiments just discussed show that a comparison between "samples" and "blanks", with and without hydrazine present, might indicate the nature of the "uncorrected interference". This was done in Table 19.

The results in Table 19 were obtained by withdrawing two samples from the feed-line and adding the "sample" reagents to them in order. During this process the appropriate calibrated overflow (Chapter 11, fig.22) was opened. When the first pair had been processed the other two flasks were taken from the feed line and the "blank" reagents added to them in order. Before "deaeration" for these tests, each reagent was separately mixed and each homogeneous solution was divided between the appropriate deaeration flasks. In this way approximately similar reagents were added to each set of comparison tests.

The order of reagent additions was:-

1st. Pair.

"Sample 1" (column B). - (1) Air-saturated water (if added). (2) Hydrazine. (3) Potassium hydroxide/iodide/iodine. (4) Manganous sulphate. (5) Sulphuric acid.

"Sample 2" (column E). - As "Sample 1" but no hydrazine addition.

2nd. Pair.

"Blank 1" (column G). - (1) Air-saturated water (if added). (2) hydrazine. (3) Potassium hydroxide/iodide/iodine. (4) Sulphuric acid. (5) Manganous sulphate.

"Blank 2" (column L). - As "Blank 1" but no air-saturated water or hydrazine additions.

The "oxygen level" in Table 19 is the sum of the analyser reading and the quantity of oxygen in the injected air-saturated water. Constant volumes of hydrazine and air-saturated water were injected and the small differences in the horizontal lines of results were due to the differences in the capacities of the sample

tubes.

Table 19 confirms and extends the results of the previous qualitative tests. It showed that the uncorrected interference was due to an oxidation in the "samples" not being duplicated in the "blanks". Although this error increased when the hydrazine and oxygen levels increased, increase in oxygen level seemed to be more significant.

The final column in Table 19 provided a check that no concealed ambiguity was producing grossly erroneous results. Although this column gave "dissolved-oxygen estimations" that were within the A.S.T.M. limits for the standard test, they were poorer than those in Chapter 11. This is probably due to the method being primarily designed to produce comparisons and there was probably an oxygen "pick-up" in the reagents used to treat the "samples without hydrazine" (mean value of 0.0005 p.p.m. - see Chapter 11). It was noticed that the " blanks" in these results showed a slight oxidation of the hydrazine when higher concentrations of free oxidant had been added.

It is difficult to assess from Table 19 whether the effect of adventitious ions brought into the samples from the "Analar" reagents can be discounted. An attempt was therefore made to increase their concentration five-fold by the use of full-strength A.S.T.M. reagents and to duplicate the tests shown in Table 19. A similar effect could have been obtained by using 2.5 ml. additions of each reagent but the "deaeration" technique had not been tested with these increments.

Table 20 shows the results obtained with the stronger reagents. The reagent additions were made in the same order as described for these of Table 19. The technique for adding the acid reagent had to be modified as it was found that, when this reagent was in the reagent-entry tube, a chocolate-brown solution formed. As this could have resulted from reaction with the polyvinyl chloride, used to attach the reagent-entry tube, the p.v.c. was replaced by polythene. The latter tubing was attached by facing it with "Araldite" adhesive (the adhesive not being in contact with the solutions). This alteration did not prevent the colouration appearing,consequently, when the acid reagent was added (in this set of experiments only) it was allowed first to remain in the reagent tube, then flushed out. This process was repeated until no colouration showed in the acid and only then was acid injected into the solution under test.

The "dissolved-oxygen estimations" in Table 20, even with the modified acid injection, are less accurate than those in Table 19. This is similar to

the observations recorded in Section 9:4 and is an independent justification of the use of dilute reagents. The observations in 9:4 were made as, in the extreme case, the iodine colour was seen in the solution but in the present experiments no colour was seen in the solutions or in the reagents. It is possible that the earlier statement in Section 9:4 should be modified to include the possibility of reagent interaction in the reagent-entry tube. This could arise from reagents being trapped in the butt-joins or the difficulty in completely flushing out the concentrated alkaline solution.

In view of the erroneous results it was impossible to use Table 20 to assess the effect of trace metals or to determine whether the differences in oxidation were due to equilibrium phenomena peculiar to the dilute reagent concentrations.

Estimations of the hydrazine remaining in the "samples" and "blanks" are shown in Table 21. The optical densities were obtained by use of a Hilgar "long-cell" absorptiometer, 20 cm. cells, and Kodak filter No.2. The hydrazine concentrations were estimated from the calibration curve shown in fig. 28, and the preparation of this curve is given in Chapter 14 which also details the reasons underlying the addition of the thiosulphate excess.

Table 21 shows that, at these oxygen levels and with the dilute reagents, hydrazine remained in both the "samples" and "blanks" at the end of the estimations. It was confirmed that more hydrazine was oxidised in the "samples" than in the "blanks", with hardly any oxidation in the latter.

The effect produced by hydrazine can be compared by a study of appropriate data from Tables 17, 19, and 21. Column 'G', Table 17, shows the errors found when a "reversed-reagents" analysis was conducted in the presence of hydrazine. A subtraction of columns 'B' and 'E', Table 19, gives a measure of the same error but this time relates it to the oxidation of hydrazine in the "Sample" of a "reversed-reagents" analysis. Column M, Table 21, measures the difference in the oxidation of hydrazine in the "Sample" and in the "Blank" of a "reversed-reagents" analysis. The data from Table 21 are increased tenfold to bring them into the same units as those from the other two tables. If now the results from equivalent concentrations of oxygen and hydrazine are compared we obtain:-

From Table 21 - 50, 90, 70, 50, 70, 60, 70, 40, 30.

From Table 19 -106, 89, 76. (Subtracting 0.0005 p.p.m. from the "oxygen recovered without hydrazine" - see Section 11:11.)

From Table 17 - 60, 106, 93, 88, 51.

These sets of results give means of 59, 90, and 80, which represent oxygen values of 0.006 p.p.m., 0.009 p.p.m., and 0.008 p.p.m. (converting hydrazine to its oxygen equivalent). This shows, considering the accuracy quoted for the A.S.T.M. method and the differing methods employed, a fair agreement. Thus the magnitude of the "uncorrected interference" seems to derive from the difference between the hydrazine oxidised in the "Sample" and that oxidised in the "Blank" of the "reversed-reagents" analysis.

The "uncorrected-interference" could be caused by oxidation of hydrazine catalysed by trace metal-ions. Table 21, however, shows there is practically no oxidation in the "Blank" and therefore the fundamental cause of the error is the failure of the added oxidant (in this case, iodine,) to oxidise the hydrazine and the subsequent difference in the oxidation in the "Sample" compared with that in the "Blank".

Potter and Everitt failed to find a suitable chemical oxidant and subsequently used an ion-exchange resin (90) to remove the hydrazine before the feed-water sampling point. This appears to be the best substantiated method of dealing with the hydrazine (and ferrous) interference when chemical analysis is undertaken. They also investigated the effect of the resin on the estimations and concluded that no reaction with dissolved oxygen occurred (at room temperature) when the test water passed through the resin even when the latter was "saturated" with hydrazine. These workers ran 500 bed volumes through a newly-regenerated resin before the first sample was taken. This overcame errors due to oxygen transfer from the air-saturated water, used in regeneration, to the sample water flowing through the resin.

The investigation of the "uncorrected interference" produced by hydrazine had shown errors of the same order as those found by Potter. If experiments on the effect of ferrous ions produced similar errors to those found by Potter then it would be indicative that Potter's experiments and the present work were measuring the same effect. The effect of ferrous interference was therefore studied and the results are shown in Table 22. These experiments were conducted in the same manner as those shown in Table 19 with ferrous ion being substituted for hydrazine. Ferrous ammonium sulphate (A.R.) was used as the source of ferrous ions. Table 22 shows that with ferrous ion also there is a decrease in the "Sample" titre which is not duplicated in the "Blank". These

results confirm the observations of Potter that ferrous ion is a source of "uncorrected interference".

The differences between the oxygen recovered in the comparison "samples" in Table 22 are not as great as those in Table 19 whilst both sets of comparison "blanks" are sensibly constant. Thus the presence of hydrazine results in a more severe "uncorrected interference" than do similar concentrations of ferrous ions. This is similar to Potter's assessment of the relative effects. The effect could be more marked in feed-water practice as the C.E.G.B. chemists, Rees and Taylor (98), give 0.01 p.p.m. as the maximum permissible concentration of iron and copper, taken together, in the feed water and Potter (ref.85, p.53) states that 0.02 p.p.m. is a hydrazine concentration which is relative to C.E.G.B. conditions.

12:4. CONCLUSIONS.

The "uncorrected-interference" encountered during the "reversed-reagents" analysis of dissolved oxygen has been found to arise from the fact that hydrazine is differentially oxidised in the "sample" and "blank" of this method. The role of trace ions, introduced with the "Analar" reagents, has been assessed and does not appear to contribute significantly to the "uncorrected interference".

An assessment of the interference due to ferrous ions has shown that the " uncorrected interference" from this source is less than that obtained from hydrazine when similar concentrations of reducing agent are compared at the same oxygen levels.

A tentative explanation of the results in Table 6 and 8 (Chapter 10) can now be given. Table 6 shows results which have an error of the same order as those in Table 17, in both cases the hydrazine concentration was 0.020 p.p.m. and the higher oxygen levels in Table 17 are approaching the oxygen levels in Table 6. Table 8 shows results in which the A.S.T.M. accuracy is approached at the lower oxygen levels and an error is beginning to appear at the higher oxygen levels. When these experiments were done it was thought that the modification in the "blank" procedure had produced acceptable results but it is now thought that this type of behaviour is consistent with the results in Table 17. In Table 17 it is shown that at low oxygen levels a "reversed-reagents" analysis can produce moderately-accurate results in the presence of hydrazine. This could have happened in Table 8 but here the situation was complicated as the apparatus could have been in such a state as

to allow the ingress of air resulting in the depression of the error which did not show up until relatively high oxygen levels were attained.

CHAPTER 13.

PRECISE ELECTROMETRIC ESTIMATION OF THE IODINE/THIOSULPHATE END-POINT.

13:1. INTRODUCTION.

In the work described in Chapter 11 the iodine released by the "Winkler" reactions was estimated potentiometrically and it is noted there that electrode "fouling" caused this method to be abandoned and a "dead-stop" end-point estimation substituted. The antecedents of this latter method have been noted in 1:5 and are expanded here. Foulk and Bawden (95) found that when a P.D. of 10-15 mv. was applied across two bright platinum wires dipping into a solution, whose iodine content was being investigated, then the current flowing when an excess of thiosulphate was present was negligible compared with that flowing when iodine was in excess. The increase in current occurred at the end-point and was easily distinguished.

Foulk and Bawden postulated that the applied voltage produced a gas film on each electrode and the hydrogen and oxygen so formed produced a concentration cell whose e.m.f. opposed the applied voltage. In the solutions under review iodide and thiosulphate depolarised the anode but "no current" flowed until the cathode was depolarised and this occurred when the end-point had been passed and free iodine was present. When the electrodes are polarised a current, sufficient to replenish the part of the gas films continually dissolved in the solution, flows. Bishop (97) has emphasised the importance of the relative electrode potentials in preference to the simple qualitative explanation given above.

Knowles and Lowden (4), (19) devised the simple circuit (fig.1) described in Section 1:5 and claimed satisfactory performance. Potter and White (ref.43 p.310) state that the high degree of discrimination, necessary for accurate dissolved-oxygen estimations, cannot be attained by a system incorporating a sensitive galvanometer as an indicator. They investigated the possibilities of heavily ballasted systems i.e. the same type as used by Bishop (96) (97), which reduce the current flowing through the solutions. A valve voltmeter was used to amplify this current and obtain reasonable indication of the end-point.

Bargh (99) has found difficulty when Potter's platinum/tungsten electrode pairs were used and replaced them by an all-platinum pair. It is possible that the tungsten electrodes may have oxidised and perhaps dipping in a sodium nitrite melt could have cleaned them. Banks (100) states that "considerable experience and manipulative skill" is needed before Potter's system gives reproducible results.

The concensus of opinion among many station chemists is similar to that expressed by Banks and a colorimetric estimation is often preferred. In the apparatus described below an unmistakable end-point indication is given and the problem of fouling by grease has been solved.

13:2. APPARATUS.

The apparatus is shown in figs.24, 25, 26. The electrical circuit is essentially that given by Potter and White (ref.6, p.310), but slightly modified for the thermionic potentiometer.

The 1.5 volt dry-cell and its associated resistors were fitted into an aluminium box. A brass terminal was fitted to this box and all earth wires were run to this terminal which was earthed to a main cold-water pipe. Even with this elaborate earthing system hand-capacitance effects occurred but were momentary and did not mask the main signal.

The electrode assembly (fig.24) was made by heating the glass tube and pinching the end into a "figure 8" shape. The prepared wire-assembly was then slipped down the tube and the end of the soda-glass tube sealed by heating. The electrodes were insulated from each other by the glass bridge formed by the "figure 8". Although the electrodes have approximated to the dimensions shown none of these dimensions has been found to be critical.

Potter and White make no mention of earthing systems but Bishop appears to have found them necessary. The experience on the present apparatus showed that the extensive screening was necessary.

The nitrogen passing through the solutions (fig.26) was of "oxygen-free" grade and was cleaned by bubbling through water. It was found that passing this nitrogen over the electrode surfaces did not increase their sensitivity but this system was retained as it effected mixing in a vertical direction.

13:3. EXPERIMENTAL PROCEDURE.

When the initial iodate/thiosulphate calibrations were carried out in pure water/potassium iodide/sulphuric acid solutions the electrode sensitivity increased with time. However, when samples were taken for a "reversed-reagents" oxygen analysis, electrode fouling soon occurred. No fouling took place when titrations were made, for an equivalent time, in a solution containing the A.S.T.M. "blank" reagents if this solution was prepared in a clean titration vessel. The fouling was therefore attributed to the silicone grease used for lubrication of the taps in the sample tubes. Potter and White employed water lubrication for the turning members of their sample tubes (fig.12c) but the ground finish in the

present taps (high-vacuum) was not smooth enough to permit this. The electrode fouling was finally traced to the silicone grease by leaving some grease overnight in an initially grease-free solution into which a non-fouled electrode was dipped. This succeeded in fouling the electrodes and a wipe with cotton wool soaked in ether gave a temporary recovery. With this apparatus the fouling was characterised by a generally sluggish response and a failure to hold the electrodes in a state of minimum current passage for more than a minute.

The final procedure which has given satisfactory results is outlined below.

(a) The thermionic potentiometer and 1.5 volt cell are both left on permanently.

(b) A new electrode assembly is "aged" by connecting up to the circuit and leaving overnight in a solution of potassium iodide/sulphuric acid/potassium iodate (the iodate is added until a pale yellow colour shows).

The potentiometer is then set for voltage readings and an excess of thiosulphate is added. When the galvanometer reading has decreased by about 80 units (initially it is set at the right-hand side of the scale i.e. "100"), an excess of iodate is added and after the galvanometer has resumed its initial reading, the process is repeated. Usually this suffices to sensitise the electrodes. The sensitivity increases to its maximum after a few titrations but the intermediate stage is still sufficient to show a clear indication of the end-point (20-30 units rise in the first minute compared with about 50 units at full sensitivity).

The electrode in use is kept connected and stored, between experiments, immersed in an iodide/acid/iodate solution.

(c) Two electrode systems are prepared and one is used whilst the other is immersed in a cleaning solution (10-15 ml. 50% potassium hydroxide in 100 ml. ethyl alcohol). When the sensitivity of the electrode in use begins to decrease the electrodes are changed over and the clean electrode is resensitised.

This cleaning process gave more consistent results than any other tried. The methods detailed in Section 9:5 were all re-attempted and the only partial success was by electrolytic gassing of the electrodes. This was obtained when the electrodes were connected to a battery which was practically discharged but subsequent attempts to clean by electrolytic decomposition of dilute acid solutions failed. Films usually formed on the electrode surfaces before they had begun to "gas" freely and uniformly. Different polarities, electrode lengths, voltage, current, and current densities were attempted without a satisfactory combination

being achieved. These films were taken to be oxides or hydroxides of platinum (101) as they were partly dissolved off when the electrodes were immersed in fairly strong iodide solutions (acidified).

(d) The normal titration procedure was to add a maximum excess of 0.1 ml. of 0.001 $\bar{N}$ thiosulphate and back-titrate with 0.01 ml. increments of 0.001 $\bar{N}$ iodate at 15 second intervals. In this way the time fluctuations, described in the next section, did not occur and a steady fall in output signal was obtained. The end-point of the back titration was indicated when the output signal ceased to fall and began to increase.

13:4. EXPERIMENTAL RESULTS.

The response of the system is shown in Table 23. The readings in this table were obtained by setting the output signal at "100" on the galvanometer when free iodine was present in the solution. The increments shown in the table were then made. When the spot approached zero it was reset to "100" by the "scale-shift" control. Thus in the table of results $2\frac{1}{2}$ scale shifts were made and the readings taken are the actual readings + approximately 250 units. As noted in Section 13:3 (d) the actual titrations for the analysis of dissolved oxygen were performed in a manner which circumvented the initial fluctuations shown after each increment and the state of the titration could be determined 15-30 seconds after an increment.

A comparison with Potter and White's preliminary standardisation was carried out with nominally 0.1 $\bar{N}$ solutions of potassium iodate and sodium thiosulphate (Hopkin and Williams "Primary volumetric standard" and "Micro analytical reagent" respectively). Each reagent was made up by weight and prepared according to normal analytical procedure. The potassium iodate was taken as the primary standard. Other solutions were:-

Starch solution; 2 g. A.R. soluble starch/200 ml. water.

Starch titration solutions; 10 ml. 0.1 N sulphuric acid, 2 ml. starch solution, 25 ml. water, 1 g. KI (A.R.).

Electrometric titration solutions; 20 ml. 0.1 $\bar{N}$ sulphuric acid, 500 ml. water, 1 g. KI (A.R.).

The results obtained with progressive dilutions are shown in Tables 24 and 25 ("exp." = normality found experimentally). In these tables the "nominal normality" of the thiosulphate and iodate are calculated according to the respective weights per litre.

Potter and White also compared the electrometric end-point and the

starch end-point using 0.1$\bar{N}$ solutions. The comparison of their results and those obtained by the present apparatus appear in Table 26.

These results show that the apparatus produces equivalent results to that used by Potter and White.

When titrating the dilute solutions, the iodine and iodate impurities in the A.R. potassium iodide were neutralised with excess thiosulphate and the solution was then brought back to the equivalence point with iodate, using the electrode system to detect the end-point. Then a known volume of thiosulphate was added and titrated with iodate.

Calibration of Circuit.

The response shown on the galvo was calibrated approximately by means of 10 megohm and 2.2 megohm resistors. These were plugged into the circuit (fig.25), one at a time, in place of the electrode system. The corresponding galvo readings were noted and the respective current and voltage readings across the 100 megohm resistance were calculated. Thus the approximate calibration of 50 galvanometer units = 30 mv. was found and a comparison made (shown below) between the end-point response in the present work and that of Potter and White's platinum/tungsten system (see ref.6, p.312 fig.10).

TIME. (secs.)	POTTER. (response in mv.)	PRESENT WORK -Table 23 (response in mv.)
0	0	0
15	0	4
60	5	29
120	16	49
180	42	60

It can be seen that the end-point response found with the present circuit is extremely positive in comparison to other circuits in which the end-points are indicated by small movements of the galvanometer.

13:5. DISCUSSION OF RESULTS.

A "reversed-reagents" oxygen estimation is calculated from the subtraction of two titres. The method just described could give a maximum error in each titration of 0.01 ml. of 0.001 $\bar{N}$ potassium iodate (the concentration used in the actual oxygen analysis). Thus a maximum error of 0.00016 p.p.m. can occur if 500 ml. samples are used. It is seldom that this maximum error would occur and a mean value of 0.0001 p.p.m. can be assumed and this is one of the factors contributing to the final precision of the analysis. When experience of the method was gained it was possible to add smaller

increments at the end-point as the proximity of the minimum value of the galvanometer readings could be estimated.

It appeared reasonable to tolerate an error rather than make more accurate estimations of the end-point by waiting a fixed time after each increment, noting the reading, and estimating each end-point graphically. The results justify the simpler method.

13:6. NOTES.

Useful pieces of ancillary equipment were 2.2 megohm and 10 megohm resistors attached to two three-pin earthed-shield plugs. In addition to their use in calibrating the output from the thermionic potentiometer they were used as a check that the output signal was normal. The check was accomplished by disconnecting the electrode system and plugging in one of the resistors. The galvanometer spot was adjusted to a fixed reading ("92" for the 2.2 megohm) and then the other resistor was substituted. The second reading should be the same as those of previous output-signal tests.

During a period of 6 months continuous use no trouble ensued from the potentiometer and on two occasions when abnormal behaviour arose it was due to a frayed earth-wire. The earthing system was then inspected regularly by visual and mechanical testing.

It has been found that the addition of 3 ml. of reagent-concentration sulphuric acid to the sample solutions aided the reproducibility of the titrations.

Each titration takes the same time and it is possible that the algebraic sums of the loss of iodine (by volatilisation) and the gain of iodine (by oxidation of the acidic iodide solutions) is the same for the "sample" as for the "blank" of the "reversed-reagents" estimation. Hence the errors due to these factors should cancel.

13:7. CONCLUSIONS.

The method described in Section 13:3 has solved the problem of electrode contamination and provides a smooth estimation of the iodine released by the Winkler reactions during an oxygen analysis.

The fact that a 36,000 ohm resistor had to be put into the circuit (fig.25) to reduce the signal shows that there is an adequate reserve of sensitivity if more accurate estimations are required in the future.

CHAPTER 14.

ESTIMATION OF HYDRAZINE.

14:1. INTRODUCTION.

Several methods of estimating hydrazine appear in the literature. It seems to be accepted that the "direct iodate" method, described by Audrieth and Ogg (82), gives satisfactory results for hydrazine when the latter is of a reasonable concentration. One electrochemical estimation of hydrazine in the range 0-0.05 p.p.m. has been described (102). This method employed a silver-platinum electrode system and a calibrated microammeter. There appears to be no further mention of this and, as most authors have estimated hydrazine colorimetrically, the amperometric estimation may have been found to be non-specific as regards hydrazine.

Two colorimetric estimations have been reported in which picryl chloride (103) or p. dimethyl-amino-benzaldehyde (88) have been used as the main reagents. These two colorimetric methods were investigated.

14:2. PREPARATION OF STANDARD HYDRAZINE SOLUTIONS.

The standard hydrazine solutions were prepared by progressive dilution.

(1) Stock solution:- A known weight of A.R. hydrazine sulphate (about 20.3 gms.) was diluted to 1 litre.

(2) Solution B:- One ml. of stock solution diluted to 1 litre.

(3) Standard solutions:- The appropriate volumes of solution B were diluted to 1 litre.

The stock solution was prepared afresh each day and stored in the dark. It was standardised in accordance with the "direct iodate" method of Audrieth and Ogg (82) and typical results are shown below.

Hydrazine in the stock solution (g./litre) according to

	(a) Weight.	(b) Volumetric analysis.	Percent. difference.
(1)	5.00	4.88	2.4%
(2)	0.89	0.88	1.1%
(3)	2.47	2.47	0%
(4)	0.89	0.87	2.2%

Thus the calculated concentrations of the "standard solutions" for the maximum difference were:-

By weight - (a) 0.0050 p.p.m. (b) 0.0100 p.p.m. (c) 0.0150 p.p.m.
(d) 0.0200 p.p.m.

By analysis-(a) 0.0049 p.p.m. (b) 0.0098 p.p.m. (c) 0.0146 p.p.m.
(d) 0.0195 p.p.m.

This discrepancy was tolerable as the desired accuracy was not better than 0.001 p.p.m.

The "Analar" specification for the hydrazine sulphate was "99% hydrazine sulphate" and the volumetric analysis gave a figure of 97.6%.

The hydrazine estimations were intended to give an indication of the mode of the "uncorrected interference" described in Chapter 11 and the desired accuracy did not justify a closer investigation of the discrepancy.

14:3. PICRYL CHLORIDE METHOD.

The method employed was that recommended by the Bayer Chemical Company (Germany) and contained in their literature on the use of hydrazine.

Reagents.

(a) 20g. of A.R. sodium citrate dissolved in 200 ml. water and added to a solution of 20g. A.R. sodium acetate dissolved in 200 ml. water.
(b) 5g. A.R. magnesium chloride in 100 ml. of water.
(c) 100 mg. A.R. sodium sulphite in 100 ml. of water.
(d) 20 mg. picryl chloride in 100 ml. of ethyl alcohol.

The ethyl alcohol (absolute) was distilled before use. Solution (c) was freshly prepared each day.

Experimental.

2 ml. of reagent (a), 1 ml. of reagent (b), 1 ml. of reagent (c), and 10 ml. of reagent (d), were added (in that order) to a 10 ml. sample of a "Standard hydrazine solution" prepared as described in Section 14:2. Preliminary experiments showed that 4 cm. cells were the minimum that could be used to measure the optical density. Therefore, to obtain a sufficient volume, duplicate samples were taken and when the colour had developed they were mixed and transferred to the cells.

The optical densities (Opt.dens.) were obtained with a "Spekker" long-cell absorptiometer, 4 cm. cells, and Kodak filter No.4.

Kodak filter No.	Opt. dens. of blank.	Opt. dens. of sample.	Opt. dens. of soln.
3	0.968	0.860	0.108
4	1.000	0.875	0.125
5	1.000	0.880	0.120

The test solutions were allowed to stand for 60 minutes in the dark and the optical densities were then measured.

Colour development time (mins.)	Optical density.
30	0.082
50	0.109
60	0.108
80	0.107

The results appear in Table 11 and in the top graph of Fig.27. The low depth of colour produced by this reagent resulted in the final reproducibility and accuracy being poor. The results obtained have a similar optical-density range to those given by Riley (103).

The reproducibility of results taken in a single day appeared better than the collected results of various days' tests. Hydrolysis of the reagent may have taken place and the alcohol was therefore dried by distillation from quicklime. The solutions turned turbid when this alcohol was used but normal behaviour was resumed when the alcohol was filtered prior to use. The turbidity was therefore attributed to unseen carry-over during the distillation. The dry, filtered alcohol did not improve the results.

14:4. p.DIMETHYL-AMINO-BENZALDEHYDE (p.D.A.B.) METHOD (88).

The standard solutions of hydrazine were prepared as described in Section 14:2.

p.D.A.B. Reagent. 0.4 g. of "Analar" p.D.A.B. was dissolved in 20 ml. ethyl alcohol (absolute) and 2 ml. of concentrated hydrochloric acid (A.R.) was added.

Method. 20 ml. of a standard hydrazine solution were added to 20 ml. of p.D.A.B. reagent, the mixture shaken, and 10 ml. of $\bar{N}$ HCl added. This was done in a 50 ml. standard flask and the solution thus prepared was designated the "sample"

The "blanks" were prepared by substituting deionised water for the standard hydrazine solutions.

The optical densities were obtained with a "Spekker" long-cell absorptiometer, 4 cm. cells, and Kodak filter No.2. The latter filter was chosen in preference to Kodak No.1 as the blank was considerably less and

enabled the measurements to be made in the more accurate range of the instrument.

Filter No.	Optical dens. of blank.	Optical dens. of sample.	Optical dens. of soln.
1	0.743	0.368	0.375
2	0.928	0.618	0.310
3	0.939	0.854	0.085

Watt and Chrisp (88) state that the colour is stable after 10 minutes. It was found that it took this time before the bubbles, formed during mixing, cleared and enabled a constant reading to be obtained.

The results (Table 10A, Fig.27) were treated with reference to the calibration line shown in fig.27, and gave a mean difference of -0.001 p.p.m. from this line (precision = 0.004 p.p.m.).

14:5. p.D.A.B. METHOD (20 cm. cells).

An attempt was made to obtain a higher precision than that reported in Section 14:4. This involved using cells with a 20 cm. light path and solutions with the same relative reagent concentrations as those given by Watt and Chrisp. The optical densities of the undernoted solutions were obtained:-

"Sample" - 100 ml. of known "hydrazine standard solution" (see Section 14:2), 100 ml. p.D.A.B. reagent, 50 ml. $\bar{N}$ HCl (A.R.).

"Blank" - 100 ml. deionised water (no hydrazine), 100 ml. p.D.A.B. reagent, 50 ml. $\bar{N}$ HCl (A.R.).

The results appear in Fig. 28 and Table 10B and show no bias about the calibration line and a precision of 0.001 p.p.m. The relevant hydrazine concentrations were calculated from the results obtained by volumetric analysis of the stock solution of hydrazine and show a difference of -0.0005 p.p.m. at the 0.020 p.p.m. level when compared with the concentrations calculated by weight.

The precision of 0.001 p.p.m. obtained for this method was considered adequate for the present work.

14:6. MODIFICATION FOR USE OF p.D.A.B. WITH WINKLER-REACTION SOLUTIONS.

In the work described in Chapter 11 it became necessary to estimate residual hydrazine in solutions containing the Winkler reagents and free iodine. Preliminary tests showed that free iodine reacted with p.D.A.B. solution and gave a coloured product. This result was obtained by the following experiments.

(1) "Test Solution". 500 ml. of deionised water containing 1g. KI (M.A.R. grade), 10 ml. dilute sulphuric acid (A.R.), and 1 ml. 0.001 $\bar{N}$ potassium iodate (P.V.S. grade).

This solution represented the iodine released in a typical oxygen analysis. The specifications of the grades of purity are given in Hopkin and William's (London) catalogue of chemical reagents.

The optical density of this test solution was found to be 0.033 units (4 cm. cells and Kodak filter No.2).

(2) Two solutions were then prepared and their optical densities measured (4 cm. cells and Kodak filter No.2).

Solution (a) - "Sample" - 20 ml. "Test Solution" (see exp.1 above), 20 ml. p.D.A.B. reagent, 10 ml. $\bar{N}$ HCl.

Solution (b) - "Blank" - 20 ml. deionised water, 20 ml. p.D.A.B. reagent, 10 ml. $\bar{N}$ HCl.

Experiment (2) gave an optical density of 0.203 for the resultant solution.

These two experiments showed that the iodine/p.D.A.B. reaction would interfere with the p.D.A.B. colorimetric estimation of residual hydrazine in the processed "samples" and "blanks" of a "reversed-reagents" oxygen analysis.

(3) "Blank solution". 500 ml. deionised water, 0.5 ml. KOH/KI/I_2, 0.5 ml. sulphuric acid, 0.5 ml. manganous sulphate, and 2.1 ml. 0.001 $\bar{N}$ thiosulphate. These reagents were those used for dissolved oxygen estimations and were added in the order written.

This "Blank solution", before the excess thiosulphate was added, had a free iodine content equivalent to 0.21 ml. of 0.001 $\bar{N}$ thiosulphate. Therefore the thiosulphate added to the "Blank solution" was sufficient to neutralise the free iodine.

Two solutions were then prepared and their optical densities measured (20 cm. cells and Kodak filter No.2).

Solution (c) - 100 ml. of "Blank solution", 100 ml. p.D.A.B. reagent, 50 ml. $\bar{N}$ HCl.

Solution (d) - 100 ml. of deionised water, 100 ml. p.D.A.B. reagent, 50 ml. $\bar{N}$ HCl.

The differences in the optical densities of solutions (c) and (d) was negligible (only 0.001 units). It can be assumed that the excess thiosulphate

neutralised the free iodine and thus prevented the iodine reacting with the p.D.A.B. to produce a coloured solution which interfered with the hydrazine estimation. The effect of the Winkler reagents was shown to be negligible.

A second standardisation of the p.D.A.B. estimation of hydrazine was then made. Instead of deionised water a solution containing the Winkler reagents plus excess thiosulphate was used. Solution M, which simulated the reagent concentrations in a dissolved oxygen analysis, was prepared by adding the reagents in the order shown.

Solution M — 1 ml. $KOH/KI/I_2$, 1 ml. sulphuric acid, 1 ml. manganous sulphate, and 1 ml. 0.1$\bar{N}$ sodium thiosulphate, all added to deionised water- the final volume being 1 litre.

The reagents used in solution M were taken from the solutions used for dissolved-oxygen analysis.

The standard hydrazine solutions were prepared as shown in Section 14:2 but the final standard solution was prepared by diluting the appropriate volume of solution B (see Section 14:2) to 1 litre with solution M (see previous paragraph). The optical densities were measured using 20 cm.cells, Filter No.2, and a "long-cell" absorptiometer. These experiments were carried out immediately after the appropriate estimations of hydrazine/p.D.A.B. in pure water (Section 14:5).

The solutions were:-

"Sample" - 100 ml. of solution M containing a known hydrazine concentration, 100 ml. p.D.A.B. reagent, 50 ml. of $\bar{N}$ HCl (Analar).

"Blank" - 100 ml. deionised water (no hydrazine), 100 ml. p.D.A.B. reagent, 50 ml. $\bar{N}$ HCl (Analar).

The results appear in Table 10B and Fig.28, and show no bias about the calibration line and a precision of 0.001 p.p.m. This was similar to that obtained with the estimations using 20 cm. cells and pure hydrazine solutions, and confirms the validity of the estimations of non-oxidised hydrazine made in Chapter 11.

CHAPTER 15.

INVESTIGATION OF A POSSIBLE NEW COLORIMETRIC ESTIMATION OF DISSOLVED OXYGEN.

15:1. INTRODUCTION.

Baker and Miles (86) found that two coal-tar phenols, 3:5-dimethylcatechol and 2:4 - dimethylresorcinol reacted in alkaline solution with dissolved oxygen to produce a red colouration. This red solution, on acidification, gave an air-stable yellow solution. The red colouration proved to be due to a sodium salt, produced by an oxidative coupling, and the yellow solution resulted from the production of the parent quinone of this sodium salt.

Experiments were made possible by the gift of small quantities of both phenols from Coalite and Chemical Products Ltd., and Professor Baker. Professor Baker also forwarded samples of the red sodium salt and information on the reaction conditions. As the quantities received were all that were available in the U.K. an evaluation of their utility in the determination of dissolved oxygen was undertaken without further purification.

15:2. PRELIMINARY TESTS.

An arbitrary small quantity of the red sodium salt was diluted with water and the optical density was taken with the "Spekker" using each of the Kodak filters in turn. A sample was acidified and the spectral range of the yellow quinone was investigated.

Filter No.	Optical Density of Red Salt.	Optical Density of Yellow Quinone.
1	0.079	2.284
2	0.215	0.262
3	0.242	0.152
4	0.255	0.045
5	0.151	
6	0.036	
7	0.009	
8	0.000	

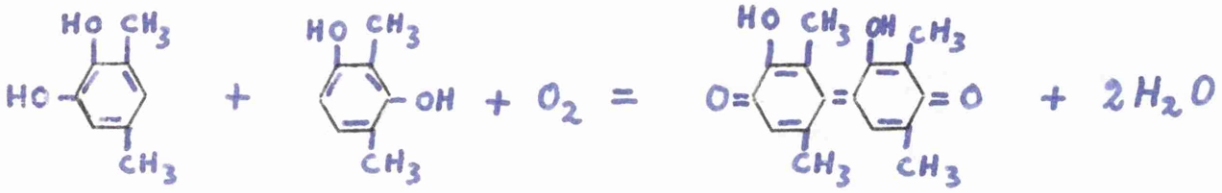
After 1 hour standing the optical density of the red salt was again taken.

Filter No.	Optical Density.
3	0.240
4	0.252

Kodak filter No.4 was chosen for the red salt measurements and filter No. 1 for the yellow quinone.

The red sodium salt was diluted to obtain an estimate of the depth of colour obtainable in the performance of dissolved oxygen estimations. At best this would only indicate the possibility of the method, and would not give an accurate standardisation, as both the purity of the salt and its degree of hydration were unknown.

Professor Baker, in a private communication, suggested that the yellow quinone could be considered formed by the reaction:-



138 g. 138 g. 32g. 272 g.

Baker and Miles (86) gave the formula of the sodium salt as $C_{16}H_{15}O_4Na$ and it was therefore considered that 32 g. oxygen was equivalent to 294 g. of the red salt.

Preliminary Standardisation.

Exp. A.

A solution of the red salt equivalent to 1.68 p.p.m. of oxygen was prepared. This is designated Solution A. 1, 2, 3, 4 and 5 ml. of water were then introduced by pipette into 25 ml. standard flasks and each flask was filled up to the mark with Solution A. The optical density of these solutions was measured in 1 cm. cells.

The yellow quinone was estimated by taking 1, 2, 3, 4 and 5 ml. of $0.2\bar{N}$ hydrochloric acid and making each up to 25 ml. with Solution A.

Exp. B.

Solution B of the red salt was made up equivalent to 0.06 p.p.m. of oxygen and diluted in the same manner as in exp. A but with 5, 50, 150, 200 and 225 ml. of water used in conjunction with 250 ml. standard flasks.

The results of experiments A and B are shown in table 9 and graphs of table 9 appear in fig. 29.

The graph shows that in the region 0-0.060 p.p.m. oxygen it is difficult to differentiate between small differences in oxygen concentrations. An estimated line has therefore been added to show the optical densities expected when the yellow quinone is estimated using 20 cm. cells.

It was expected, from the graphs in fig. 29 that estimations of the yellow quinone in the range 1.3 - 1.7 p.p.m. of dissolved oxygen would only be accurate to approximately 0.1 p.p.m. In the range 0-0.060, using 20 cm. cells, an accuracy of 0.003 p.p.m. seemed possible.

Solutions equivalent to air-saturated water (10 p.p.m. of oxygen) could not be measured directly due to their high optical density. It would be possible to do so with micro-cells. However when the red salt solutions, equivalent to 10 p.p.m. of oxygen, were acidified with hydrochloric acid a precipitate was formed. This was tested for chloride and a negative result was obtained, showing that the precipitate was not a hydrochloride. The precipitate was attributed to a solubility effect as, when $2\bar{N}$ acetic acid was used for the neutralisation the precipitate still appeared, but when glacial acetic was used no precipitate was formed.

The red coloured solutions only changed their optical density by 1% in 3 hours.

15:3. EVALUATION OF METHOD.

The preliminary tests showed that for dissolved oxygen in the region 0-0.060 p.p.m., 20 cm. cells and filter No.1 were most suitable for the measurement of the colour density of the yellow quinone.

Solutions.

(a) 0.06 g. 2:4 - dimethylresorcinol in 100 ml. of water and slightly acidified with sulphuric acid.
(b) 0.06 g. 3:5 - dimethylcatechol made up as in (a).
(c) $2\bar{N}$ sodium hydroxide.
(d) $3\bar{N}$ sulphuric acid.

The apparatus in which dissolved oxygen was estimated in pure water and in water containing hydrazine, was employed for these tests (see Chap.10). The procedure was as already described and the reagents were deaerated in the side necks before use. The reagents were added as follows:-

Order of reagent addition	Sample	Blank
(1)	Air-saturated water	-
(2)	(c)	(c)
(3)	(a)	(d)
(4)	(b)	(a)
(5)	(d)	(b)

The optical densities of the sample and blank were each compared with the optical density of distilled water. The optical density of the particular oxygen concentration studied was obtained by subtraction of these two results. This overcomes any error arising from deterioration in colour due to the time lag in the fixing of the sample and blank.

Test	Oxygen Concentration.	Optical Density.
1	Nil	0.021
2	0.006 p.p.m.	0.020

When the solutions from these tests were added to air-saturated water and made alkaline a deep-red colour was obtained. This showed that sufficient phenol reagents were present.

A test was then carried out to find out at which oxygen concentration the red sodium salt appeared visually.

Test	Oxygen Conc.(p.p.m.)	Volume of each phenol added (ml.)	Red colour
3	0.018	2	None
4	0.036	2	None
5	0.036	4	None
6	0.018	4	None

However, in test 5, when about 12 $\bar{N}$ sodium hydroxide was added a red colour was obtained. Test 6 was then carried out with 12 $\bar{N}$ sodium hydroxide but no visual colour was obtained.

Another series of tests, similar to tests 3-6, were performed with saturated sodium hydroxide as reagent (c), 2 ml. of each phenol being added.

Test.	Oxygen conc. (p.p.m.)	Appearance of "red-salt" colour.
7	0.018	very faint pink
8	0.036	faint pink
9	0.054	definitely pink

When test 9 was acidified (75% acid) a slightly yellow colour was obtained.

Tests 10 and 11 were then performed using the reagents of tests 7-9 and allowing the red colour to develop for 15 minutes before acidification. the yellow colour was then estimated.

Test.	Oxygen conc.(p.p.m.)	Optical density of yellow solution.
10	0.016	0.107
11	0.032	0.143

These results were disappointing as test 11 would be expected to give an optical density of 0.214.

Tests (12 and 13) were now carried out to verify that results 10 and 11 were because the method was non reproducible and not due to a threshold value of oxygen being necessary before colour developed. These tests were duplicated regarding reaction conditions. The red colour was allowed to develop 25 minutes before acidification (the optimum time) 12$\bar{N}$ sodium hydroxide and 18$\bar{N}$ sulphuric acid were used as reagents (c) and (d).

Test	Oxygen conc.(p.p.m.)	Optical density of yellow colour.
12	0.015	0.126
13	0.015	0.053

Further tests on this method were carried out utilising the sample tubes and general technique described in Chapter 11, the apparatus arrangement being shown in fig. 22. The oxygen level of the flow from the deaerator was recorded on the Cambridge analyser and appropriate volumes of air-saturated water were added to the samples after they had been removed from the feed-line. The results are shown in Table 9B. These results were obtained with the samples and blanks being processed as given in Section 11:7. The optical density of the colour was measured with a Hilger long-cell absorptiometer (20 cm. cells and Kodak filter No.1). The relevant concentrations and time between the addition of alkali and the final acidification are shown below.

(D.M.C. = 3:5 dimethyl catechol and D.M.R. = 2:4 dimethyl resorcinol.)

Table 9B, series A.

D.M.R. = 0.6 g./1r. (slightly acidified with sulphuric acid).
D.M.C. = 0.64g./1r. (" " " ").
Sodium hydroxide = 12$\bar{N}$.
Sulphuric acid = 18$\bar{N}$.
Reagent additions = 0.7 ml. of each.
10 minutes reaction in alkaline solution.

Table 9B, series B.

D.M.R. = 5.0 g./1r. (slightly acidified).
D.M.C. = 4.9 g./1r. (" ").
Sodium hydroxide = 12$\bar{N}$.
Sulphuric acid = 18$\bar{N}$.
Reagent additions = 0.7 ml. of each.
10 minutes reaction in alkaline solution.

Table 9B, series C.

D.M.R. = 5.0 g./1r. (slightly acidified).
D.M.C. = 4.9 g./1r. (" ").
Sodium hydroxide = 12$\bar{N}$.
Sulphuric acid = 18$\bar{N}$.
Reagent additions = 0.7 ml. of phenols and 2 ml. of alkali and acid.
20 minutes reaction in alkaline solutions.

When any of the solutions measured in table 9B were shaken in air and then made alkaline a deep red colour was obtained.

15:4. CONCLUSIONS.

The results in table 9B show that there is an increase in the optical density associated with increase in the oxygen level of the solutions. Neither the increase in the reaction time nor the increase in the concentration of reagents seemed to improve the depth of colour produced. The reproducibility and the optical densities of the colours produced are such that an analysis of low oxygen ranges could not be conducted with any confidence.

CONCLUSION.

It appears inevitable that, with the advent of generating stations operating in the supercritical region, the present specifications for dissolved oxygen estimations will be reviewed and more accurate estimations demanded. The second type of apparatus, developed in this work, has been shown to be capable of satisfying this. It is held, however, that the time has come when a strict investigation should be carried out to discover the oxygen levels that can be tolerated at certain temperatures and pressures. The only rule which is at present applied is that the "oxygen level should be as low as possible".

It would seem that the modifications to the classical Winkler technique, which are now available, can satisfy future demands for greater precision in dissolved oxygen estimations.

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TABLE 1.

Absorption Spectrum of Oxidised O-Tolidine Solution

Wavelength (mμ.)	Optical density	Wavelength (mμ.)	Optical density.
490	0·020	436	0·160
485	0·026	435	0·161
480	0·032	430	0·154
475	0·042	425	0·134
470	0·054	420	0·129
465	0·070	415	0·114
460	0·082	410	0·099
455	0·108	405	0·082
450	0·130	400	0·070
445	0·150	395	0·056
440	0·160	390	0·045

TABLE 2.

Optical density of ceric sulphate/o-tolidine solutions calculated as the equivalent dissolved oxygen values.

20 cm. cells.

Dissolved oxygen. (p.p.m. x 10^{-3})	Optical density.	Dissolved oxygen. (p.p.m. x 10^{-3})	Optical density.
2·5	0·01	10·5	0·32
5	0·065	10·5	0·325
7·5	0·19	4·5	0·025
10	0·30	6·5	0·095
12·5	0·39	8·5	0·19
17·5	0·59	15	0·465
25	0·855	17	0·545
		21·5	0·735

4 cm. cells.

Dissolved oxygen. (p.p.m. x 10^{-3})	Optical density.	Dissolved oxygen. (p.p.m. x 10^{-3})	Optical density.
10	0·07	4·5	0·005
20	0·145	8·5	0·04
25	0·20	13	0·085
34.5	0·29	21·5	0·175
49·5	0·42	30	0·26
59·5	0·535	43	0.385
74·5	0·60	55·5	0·50
		64	0·57

TABLE 3.

Acid added (ml.)	Optical density. (4 cm.cells).
1	0·395
2	0·403
3	0·405
4	0·394
5	0·394

TABLE 4.

TIME		Optical density.	TIME		Optical density.
Mins.	Secs.		Mins.	Secs.	
0	52	0·187	3	37	0·189
1	22	0·192	4	27	0·188
1	45	0·191	4	55	0·188
2	6	0·190	5	47	0.187
2	44	0·189	6	16	0·187
3	11	0·189			

TABLE 5.

Dissolved oxygen injected ($p.p.m. \times 10^3$).	Dissolved oxygen measured ($p.p.m. \times 10^3$).	Difference ($p.p.m. \times 10^3$).
0	0	0
0	1	+ 1
0	1	+ 1
0	0	0
0	1	+ 1
0	- 3	- 3
0	1	+ 1
0	- 1	- 1
5	5	0
6	7	+ 1
6	6	0
6	8	+ 2
12	14	+ 2
15	18	+ 3
17	16	- 1
18	17	- 1
18	18	0
26	28	+ 2
27	29	+ 2
27	26	- 1
28	23	- 5
28	26	- 2
35	38	+ 3
36	34	- 2
36	36	0
37	36	- 1
37	37	0
48	48	0
48	49	+ 1
49	46	- 3

TABLE 6 .

Results in presence of hydrazine with non-modified blank.

Dissolved oxygen added (p.p.m. x 10^3.)	Dissolved oxygen measured (p.p.m. x 10^3.)	Difference (p.p.m. x 10^3.)	Contact time before Mn^{++} added (mins.)
18	14	- 4	1·5
18	10	- 8	1·5
18	10	- 8	1·5
20	10	- 10	3
20	12	- 8	3
18	10	- 8	3
16	10	- 6	3
20	10	- 10	6
18	10	- 8	6
18	10	- 8	6
18	14	- 4	30
20	8	- 12	30
18	10	- 8	30

TABLE 7.

Comparison of results in presence of hydrazine and those obtained with pure water.

Dissolved oxygen added (p.p.m.x 10^3.)	Dissolved oxygen measured (p.p.m.x 10^3.)	Difference (p.p.m.x 10^3.)	Sample titre (ml.)	Blank titre (ml.)	Contact time if hydrazine added (mins.)
18	14	- 4	0.38	0·21	1·5
18	18	0	0·425	0.205	-
18	10	- 8	0·22	0·09	1·5
18	18	0	0·295	0·08	-
20	10	- 10	0·155	0·04	6
18	22	+ 4	0·36	0·09	-

TABLE 8.

Results obtained in presence of hydrazine using modified blank.

Dissolved oxygen added ($p.p.m. \times 10^3$.)	Dissolved oxygen measured. ($p.p.m. \times 10^3$.)	Difference ($p.p.m. \times 10^3$.)
0	2	+ 2
0	3	+ 3
0	1	+ 1
0	2	+ 2
5	6	+ 1
5	5	0
5	7	+ 2
6	6	0
8	8	0
11	9	- 2
12	10	- 2
13	15	+ 2
16	15	- 1
16	11	- 5
16	13	- 3

TABLE 9A.

Optical densities of various concentrations of the red sodium salt and the yellow quinone, both expressed as their equivalent oxygen values.

Exp. A - 1 cm. cells.

Oxygen conc.(p.p.m.)	Optical density of red salt.	Optical density of yellow quinone.
1·68	1·065	
1·61	1·022	0·424
1·55	0·972	0·406
1·48	0·933	0·385
1·41	0·892	0·372
1·35	0·846	0·358

Exp. B - 4 cm. cells.

Oxygen conc.(p.p.m.)	Optical density of red salt.	Optical density of yellow quinone.
0·06	0·237	
0·059		0·090
0·048	0·193	0·075
0·024	0·095	0·040
0·012	0·042	0·024
0·006	0·028	0·012

Oxygen conc.(p.p.m.)	Optical density of yellow quinone (4 cm.cells.)	Optical density estimated for 20 cm. cells.
0·059	0·090	0·450
0·048	0·075	0·375
0·024	0·040	0·200
0·012	0·024	0·120
0·006	0·012	0·060

TABLE 9B.

Density of Colour Produced by the Reaction of Dimethyl-cathechol and Dimethyl-resorcinol with Dissolved Oxygen.

	Dissolved oxygen. (p.p.m. x 10^4)	Optical density.		Dissolved oxygen. (p.p.m. x 10^4)	Optical density.
Series A.	71	0.007	Series B.	141	0.030
	78	0.015		156	0.012
	78	0.009		157	0.021
	146	0.028			
	162	0.039	Series C	141	0.020
	163	0.047		157	0.025
				158	0.029

TABLE 10A.

Optical density of hydrazine/p.dimethyl-amino benzaldehyde complex.

Hydrazine (mg./lr.)	Optical density.	Hydrazine (mg./lr.)	Optical density.
0·026	0·054	0·100	0.206
0·028	0·068	0·099	0.211
0·025	0·047	0·124	0·269
0·050	0·106	0·125	0·257
0·050	0·118	0·141	0·309
0·064	0·144	0·149	0·305
0·071	0·157	0·149	0·328
0·075	0·136	0·128	0·256
0·193	0·369	0·212	0·412

TABLE 10B.

Optical density of hydrazine/p.D.A.B. complex.

(20 cm. cells, Kodak filter No.2.)

(a) Ordinary Calibration.

Hydrazine. (p.p.m.)	Optical density.	Hydrazine. (p.p.m.)	Optical density.
0.019 (5)	0.176	0.009 (8)	0.100
	0.191		0.100
	0.197		0.094
	0.195		0.094
0.014 (6)	0.160	0.004 (9)	0.043
	0.162		0.048
	0.165		0.059
	0.170		0.076

(b) Calibration with Winkler Reagents + excess Thiosulphate.

Hydrazine. (p.p.m.)	Optical density.	Hydrazine. (p.p.m.)	Optical density.
0.019 (5)	0.198	0.009 (8)	0.096
	0.206		0.110
	0.223		0.105
	0.212		0.098

TABLE 11.

Optical density of hydrazine/picryl chloride complex.

(4 cm. cells)

Hydrazine (mg./lr.)	Optical density.	Hydrazine (mg./lr.)	Optical density.
0·022	0·025	0·088	0·075
0·044	0·051	0·106	0·066
0·044	0·025	0·106	0·066
0·053	0·028	0·132	0·103
0·066	0·048	0·133	0·105
0·072	0·041	0·144	0·083
0·088	0·042		

TABLE 12.

Response of Meter to an Increase of 0.0014 p.p.m. of Dissolved Oxygen

(Results expressed as p.p.m. x 10^4 of dissolved oxygen)

Time (mins.)	Meter Reading	Time (mins.)	Meter Reading	Time (mins.)	Meter Reading
0	0	3	3	10	9
$\frac{1}{4}$	0	$3\frac{1}{2}$	3	12	10
$\frac{1}{2}$	0	4	4	14	11
$\frac{3}{4}$	0+	5	5	16	11
1	1	6	5	24	13
$1\frac{1}{2}$	1	7	6	35	14
2	1	8	7	75	14
$2\frac{1}{2}$	2	9	8		

TABLE 13.

Comparison of Dissolved Oxygen in Feed Water as Measured by Cambridge Meter and Chemical Method.

(All results expressed as p.p.m. x 10^4 of dissolved oxygen)

Chemical Analysis.

Sample	Blank	Dissolved oxygen recovered (A-B).	Meter reading	Dissolved oxygen added.	Oxygen level (D+E).	(C-F)
A	B	C	D	E	F	G
262	160	102	16	108	124	-22
81	70	11	22	0	22	-11
148	141	7	15	0	15	-8
58	42	16	21	0	21	-5
59	42	17	21	0	21	-4
63	58	5	9	0	9	-4
80	63	17	20	0	20	-3
98	85	13	16	0	16	-3
50	39	11	13	0	13	-2
310	173	137	16	122	138	-1
45	33	12	13	0	13	-1
82	72	10	9	0	9	+1

TABLE 13.(Contd.)

Sample	Blank	Dissolved oxygen recovered (A-B).	Meter reading	Dissolved oxygen added	Oxygen level (D+E).	(C-F).
A	B	C	D	E	F	G
27	8	19	17	0	17	+2
65	41	24	22	0	22	+2
80	65	15	13	0	13	+2
72	50	22	20	0	20	+2
93	75	18	15	0	15	+3
68	50	18	15	0	15	+3
75	50	25	20	0	20	+5
284	157	127	15	106	121	+6
67	42	25	16	0	16	+9
173	32	141	16	110	126	+15
110	77	33	15	0	15	+18
164	135	29	19	0	19	+10

TABLE 14.

Recovery of Dissolved Oxygen

(Results expressed as p.p.m. x 10^4 of dissolved oxygen)

Chemical Analysis						
"Total oxygen"	"Base-level oxygen	Oxygen recovered (A-B)	Meter reading	Oxygen added	Oxygen level (D+E)	(C-E)
A	B	C	D	E	F	G
68	70	-2	15	0	15	-2
50	55	-5	15	0	15	-5
70	75	-5	15	0	15	-5
50	62	-12	15	0	15	-12
102	108	-6	20	0	20	-6
90	97	-7	20	0	20	-7
63	70	-7	16	0	16	-7
64	72	-8	20	0	20	-8
33	41	-8	17	0	17	-8
78	91	-13	20	0	20	-13
53	18	35	25	49	74	-14
99	31	68	23	54	77	+14
129	68	61	22	57	79	+4
132	83	49	15	60	75	-11

TABLE 14.(Contd.)

"Total oxygen"	"Base-level oxygen	Oxygen recovered (A-B)	Meter reading	Oxygen added	Oxygen level (D+E)	(C-E)
A	B	C	D	E	F	G
117	51	66	15	73	88	-7
139	48	91	15	102	117	-11
308	201	107	15	115	130	-8
202	53	149	18	144	162	+5
205	59	146	25	148	173	-2
226	65	161	25	163	188	-2
232	64	168	26	166	192	+2

TABLE 15.

Comparison of Data from Various Methods

A. Recovery of dissolved oxygen by Potter and White (ref.2, p.328)

Data computed from ("Dissolved oxygen recovered by chemical analysis" - "Actual increase in dissolved oxygen").

Mean of differences (accuracy) = - 0.0003 p.p.m.

Standard Deviation (precision) = 0.0007 p.p.m.

B. Recovery of dissolved oxygen (Table 14)

Data computed as above i.e. from Table 14, column G.

Mean of differences (accuracy) = -0.0005 p.p.m.

Standard deviation (precision) = 0.0007 p.p.m.

C. Comparison with electrochemical analyser (Table13).

Data computed from ("Dissolved oxygen recovered by chemical analysis" - "Oxygen level").

Mean of differences (accuracy) = +0.0001 p.p.m.

Standard deviation (precision) = 0.0008 p.p.m.

TABLE 16.

Dissolved-Oxygen Content of Air-Saturated Reagents

(Results are expressed as mg. x 10^4 of dissolved oxygen)

Sample	Meter reading	(A-B)	Blank	Oxygen added with 0.6 ml. of both reagents (C-D)
A	B	C	D	F
83	9	74	2	72
85	10	75	2	73
86	11	75	2	73
96	10	86	6	80
91	11	80	6	74
97	10	87	14	73
99	11	88	13	75
99	10	89	14	75
99	11	88	12	76
85	10	75	1	74
				Mean = 74.5

TABLE 17

Recovery of Dissolved Oxygen in the Presence of Hydrazine

(Results expressed as p.p.m. x 10^4 of dissolved oxygen with the exception of the hydrazine concentrations which are expressed as p.p.m. x 10^3 of hydrazine).

Chemical Estimation							Hydrazine Concentrations	
Sample	Blank	Oxygen recovered (A - B)	Meter reading	Oxygen added to sample	Oxygen level of sample (D + E)	Oxygen difference (C - F)	Sample	Blank
A	B	C	D	E	F	G		
114	79	35	15	0	15	+ 20	19	18
73	26	47	16	0	16	+ 31	19	18
53	48	5	20	0	20	- 15	20	20
57	43	14	20	0	20	- 6	20	20
64	46	18	20	0	20	- 2	20	20
28	8	20	20	0	20	0	20	20
34	18	16	17	43	60	- 44	19	18
95	33	62	18	43	61	+ 1	18	19
66	49	17	18	45	63	- 46	18	19
52	20	32	19	47	66	- 34	20	20
83	34	49	18	49	67	- 18	20	20

Continued

TABLE 17

continued

Chemical Estimation							Hydrazine Concentrations	
Sample	Blank	Oxygen recovered (A - B)	Meter reading	Oxygen added to sample	Oxygen level of sample (D + E)	Oxygen difference (C - F)	Sample	Blank
A	B	C	D	E	F	G		
79	53	26	18	52	70	- 44	20	20
37	1	36	22	57	79	- 43	20	19
123	87	36	15	65	80	- 44	20	20
104	71	33	15	78	93	- 60	20	20
76	66	10	12	104	116	-106	18	19
115	78	37	12	118	130	- 93	20	20
122	75	47	14	121	135	- 88	20	20
102	56	46	14	120	134	- 88	19	18
100	20	80	15	116	131	- 51	20	20

TABLE 18

Variation in the Order of Reagent Additions to Parallel Samples and its Effect on Hydrazine Oxidation.

(These iodine-titration results are expressed as p.p.m. x 10^4 of dissolved oxygen and the sub-table headings show the order of reagent additions).

TABLE 18A

(a)	Nil air-saturated water.	(a)	Nil air-saturated water
(b)	0.018 p.p.m. N_2H_4	(b)	0.019 p.p.m. N_2H_4
(c)	$KOH/KI/I_2$	(c)	H_2SO_4
(d)	H_2SO_4	(d)	$KOH/KI/I_2$
	12		12

Oxygen level of feed-water = 0.0020 p.p.m. (meter)

TABLE 18B

(a)	0.6 ml air-saturated water	(a)	0.6 ml air-saturated water
(b)	N_2H_4	(b)	N_2H_4
(c)	$KOH/KI/I_2$	(c)	H_2SO_4
(d)	H_2SO_4	(d)	$KOH/KI/I_2$

"O_2" found	O_2 level of feed-water (meter)	N_2H_4 added (p.p.m. x 10^3)	"O_2" found	O_2 level of feed-water (meter)	N_2H_4 added (p.p.m. x 10^3)
17	20	18	20	20	19
21	20	20	23	20	20
30	15	20	28	15	20
32	15	18	30	15	20
32	15	18	30	15	19

TABLE 18C

(a) Nil air-sat'd H_2O.	(a) Nil air-sat'd H_2O	(a) Nil air-sat'd H_2O	(a) Nil air-sat'd H_2O
(b) 0.022 p.p.m. N_2H_4	(b) Nil N_2H_4	(b) 0.020 p.p.m. N_2H_4	(b) Nil N_2H_4
(c) $KOH/KI/I_2$	(c) $KOH/KI/I_2$	(c) H_2SO_4	(c) H_2SO_4
(d) H_2SO_4	(d) H_2SO_4	(d) $KOH/KI/I_2$	(d) $KOH/KI/I_2$
38	36	30	33

Oxygen level of feed-water = 0.0015 p.p.m.

TABLE 18D

(a) 0.6 ml air-sat'd. H_2O	(a) 0.6 ml air-sat'd H_2O
(b) 0.020 p.p.m. N_2H_4	(b) Nil N_2H_4
(c) A.S.T.M. "Sample" reagents in order	(c) A.S.T.M. "Sample" reagents in order
125	200
98	226
As above but no air-sat'd H_2O added. (Meter reading = 0.0015 p.p.m.)	As above but no air-sat'd H_2O added. (meter reading = 0.0015 p.p.m.
61	102

TABLE 18E

(a) 0.6 ml air-sat'd H_2O	(a) 0.6 ml air-sat'd H_2O
(b) 0.018 p.p.m. N_2H_4	(b) Nil N_2H_4
(c) A.S.T.M. "Blank" reagents in order	(c) A.S.T.M. "Blank" reagents in order
29	35
8	8

TABLE 18E - continued

as above but no air-sat'd H_2O added. (meter reading = 0.0015 p.p.m.)	as above but no air-sat'd H_2O added. (meter reading = 0.0015 p.p.m.)
29	33

TABLE 19

The Effect of Hydrazine on the Modified A.S.T.M. "Sample" and "Blank"

(Results are expressed as p.p.m. x 10^4 of dissolved oxygen except where otherwise stated).

A.S.T.M. "Sample" with hydrazine			A.S.T.M. "Sample" without hydrazine		A.S.T.M. "Blank" with hydrazine			A.S.T.M. "Blank" without hydrazine		
O_2 level	O_2 found (+ I_2)	N_2H_4 (p.p.m x 10^3)	O_2 level	O_2 Found (+ I_2)	O_2 level	O_2 Found (+ I_2)	N_2H_4 (p.p.m. x 10^3)	O_2 level	O_2 Found (+ I_2)	(E-L)-D
A	B	C	D	E	F	G	H	K	L	
20	34	20	20	47	20	14	18	20	17	+ 10
21	15	20	21	44	21	14	19	21	13	+ 10
20	30	20	20	76	20	27	19	20	42	+ 14
144	70	20	143	181	128	9	18	18	9	+ 29
151	77	20	151	171	136	10	18	22	11	+ 9
130	81	18	136	162	146	13	20	21	18	+ 8
20	36	61	20	73	21	23	57	21	40	+ 13
20	48	61	20	70	20	33	54	20	44	+ 6
21	57	61	21	78	21	35	54	21	45	+ 12
18	46	61	18	75	18	38	57	18	49	+ 8
149	75	61	148	172	133	2	54	18	4	+ 20
151	33	61	150	181	135	1	54	20	2	+ 29
114	55	61	113	139	102	4	54	17	21	+ 5
117	69	61	116	170	105	9	54	18	41	+ 13

TABLE 20

Results obtained with Full-Strength A.S.T.M. Reagents

(Results are expressed as p.p.m. x 10^4 of dissolved oxygen except where otherwise stated).

A.S.T.M. "Sample" with hydrazine			A.S.T.M. "Sample" without hydrazine		A.S.T.M. "Blank" with hydrazine			A.S.T.M. "Blank" without hydrazine		
O_2 level	O_2 found (+ I_2)	N_2H_4 (p.p.m. x 10^3)	O_2 level	O_2 found (+ I_2)	O_2 level	O_2 found (+ I_2)	N_2H_4 (p.p.m. x 10^3)	O_2 level	O_2 found (+ I_2)	(E-L)-D
A	B	C	D	E	F	G	H	K	L	
130	141	20	129	246	116	47	18	16	56	+ 61
123	132	20	124	208	111	19	18	16	30	+ 54
131	105	20	130	208	117	7	18	16	45	+ 33
131	126	20	130	159	117	5	18	14	11	+ 18
134	116	20	133	148	119	3	18	15	2	+ 13
133	130	20	132	151	119	- 2	18	17	0	+ 19
129	85	20	129	141	116	3	18	20	12	0

TABLE 21

Estimation of Hydrazine which Remains after Dissolved Oxygen Analysis.

(Hydrazine concs. are expressed as p.p.m. x 10^3)

Additions in order "SAMPLE"				Additions in order "BLANK"				
(a) Test Water. (b) 0.6 ml. air-satd. water. (c) 0.02 p.p.m. N_2H_4. (d) $KOH/KI/I_2$. (e) $MnSO_4$. (f) H_2SO_4. (g) 0.1 ml. of 0.1N thiosulphate.				(a) Test Water. (b) 0.6 ml. air-satd. water. (c) 0.02 p.p.m. N_2H_4. (d) $KOH/KI/I_2$. (e) H_2SO_4. (f) $MnSO_4$. (g) 0.1 ml. of 0.1N thiosulphate.				
Actual N_2H_4 added	Optical density of complex.	Estim. of unreacted N_2H_4	Oxidised N_2H_4 (A - C)	Actual N_2H_4 added.	Optical density of complex.	Estim. of unreacted N_2H_4	Oxidised N_2H_4 (E - G)	D-K
A	B	C	D	E	F	G	K	M
20	0.095	9	11	20	0.145	14	6	5
20	0.094	9	11	20	0.186	18	2	9
20	0.140	13	7	20	0.231	22	0	7
20	0.137	13	7	20	0.187	18	2	5
20	0.118	11	9	20	0.190	18	2	7
20	0.140	13	7	20	0.198	19	1	6
18	0.094	9	9	19	0.180	17	2	7
18	0.103	10	8	19	0.151	15	4	4
18	0.145	14	4	19	0.190	18	1	3

The probable oxygen-level of each test was between 0.010 and 0.014 p.p.m.

TABLE 22

The Effect of Ferrous Ions on the Modified A.S.T.M. "Sample" and "Blank"

(Results are expressed as p.p.m. x 10^4 of dissolved oxygen except where otherwise stated).

A.S.T.M. "Sample" with Fe^{++}			A.S.T.M. "Sample" without Fe^{++}		A.S.T.M. "Blank" with Fe^{++}			A.S.T.M. "Blank" without Fe^{++}		
O_2 level	O_2 found (+ I_2)	Fe^{++} (p.p.m. x 10^3)	O_2 level	O_2 found (+ I_2)	O_2 level	O_2 found (+ I_2)	Fe^{++} (p.p.m. x 10^3)	O_2 level	O_2 found (+ I_2)	(R-Y)-Q
M	N	P	Q	R	S	T	V	W	Y	
140	159	20	139	190	126	32	18	18	38	+ 13
144	171	20	145	193	136	36	19	20	37	+ 12
148	166	20	147	202	132	33	18	20	30	+ 25
142	150	20	143	185						

TABLE 23.

Response of Platinum/Platinum

Electrode System.

(Units quoted are galvanometer scale units)

Time After reagent addition (mins.)	0.1 ml. of 10^{-3} N thiosulphate added.	Further .01 ml. of 10^{-3} N thiosulphate added.	0.01 ml. 10^{-3} N iodate added.	Further 0.01 ml. 10^{-3} N iodate added.	Further 0.01 ml. of 10^{-3} N iodate added.
0	361	376	93	89	95
$\frac{1}{4}$	300	310	103	91	102
$\frac{1}{2}$	289	280	105	95	119
$\frac{3}{4}$	253	240	104	98	133
1	240	215	102	99	143
$1\frac{1}{2}$	214	182	97	100	159
2	202	162	93	98	177
$2\frac{1}{2}$	197	150	90	97	190
3	196	142	89	95	197
4	200	131			216
State of Solution	Before end-point	Over end-point	Before end-point	Before end-point	Over end-point

(50 galvo units approximately equals 30 mv.)

TABLE 24.

	NORMALITIES							
Solution	Nominal	Exp.	Nominal	Exp.	Nominal	Exp.	Nominal	Exp.
KIO_3	0.10003	-	0.10003	-	0.01000	-	0.00100	-
$Na_2S_2O_3$	0.10000	0.10021	0.10000	0.10012	0.01000	0.01000	0.00100	0.00100
"		0.10039		0.10021		0.01000		0.00100
"		0.10012		0.10021		0.01000		0.00098
Mean		0.10024		0.10018		0.01000		0.00099
	Starch		Electrical End-Points.					

Exp. = Normalities obtained by experiment.

TABLE 25

Nominal Normality	POTTER		PRESENT RESULTS	
	Mean Experimental Normality	Theoretical Normality	Mean Experimental Normality	Theoretical Normality
10^{-1}	1.20×10^{-1}	-	1.00×10^{-1}	-
10^{-2}	1.20×10^{-2}	1.20×10^{-2}	1.00×10^{-2}	1.00×10^{-2}
10^{-3}	1.19×10^{-3}	1.20×10^{-3}	0.99×10^{-3}	1.00×10^{-3}

TABLE 26

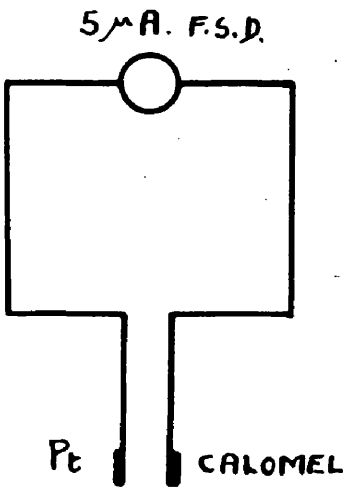
Estimation of Normality of 0.1$\bar{N}$ $Na_2 S_2 O_3$

							Mean
Potter -	Starch	0.1197	:	0.1200	:	0.1196	: 0.1198
Results of Table 24	Starch	0.1002	:	0.1004	:	0.1001	: 0.1002
Potter -	Electrical	0.1204	:	0.1200	:	0.1192	: 0.1199
Results of Table 24	Electrical	0.1001	:	0.1002	:	0.1002	: 0.1002

Table 25 - Comparison of present results and Potter's (Ref.6,p.314) for standardisation of sodium thiosulphate.

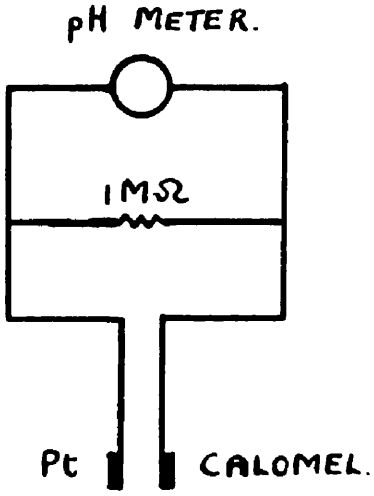
Table 26 - Comparison of present results and Potter's (Ref.6, p.313)

KNOWLES & LOWDEN.



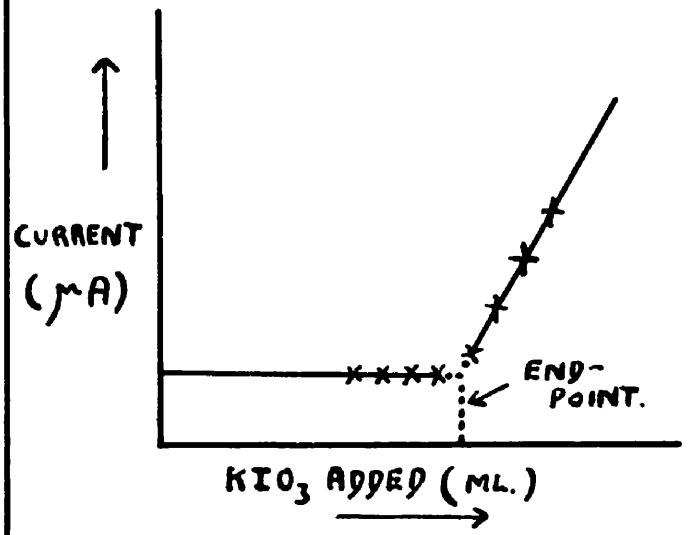
(a)

YOUNG.



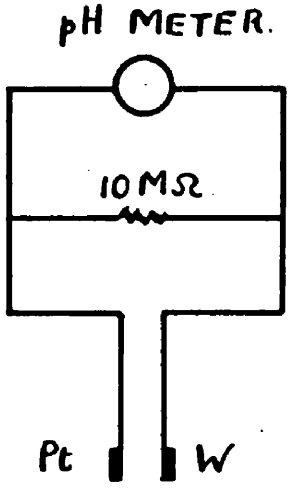
(b)

KNOWLES & LOWDEN – BACK TITRATION CURVE.



(d)

POTTER



(c)

FIG 1

Cambridge Analyser.
— Schematic.

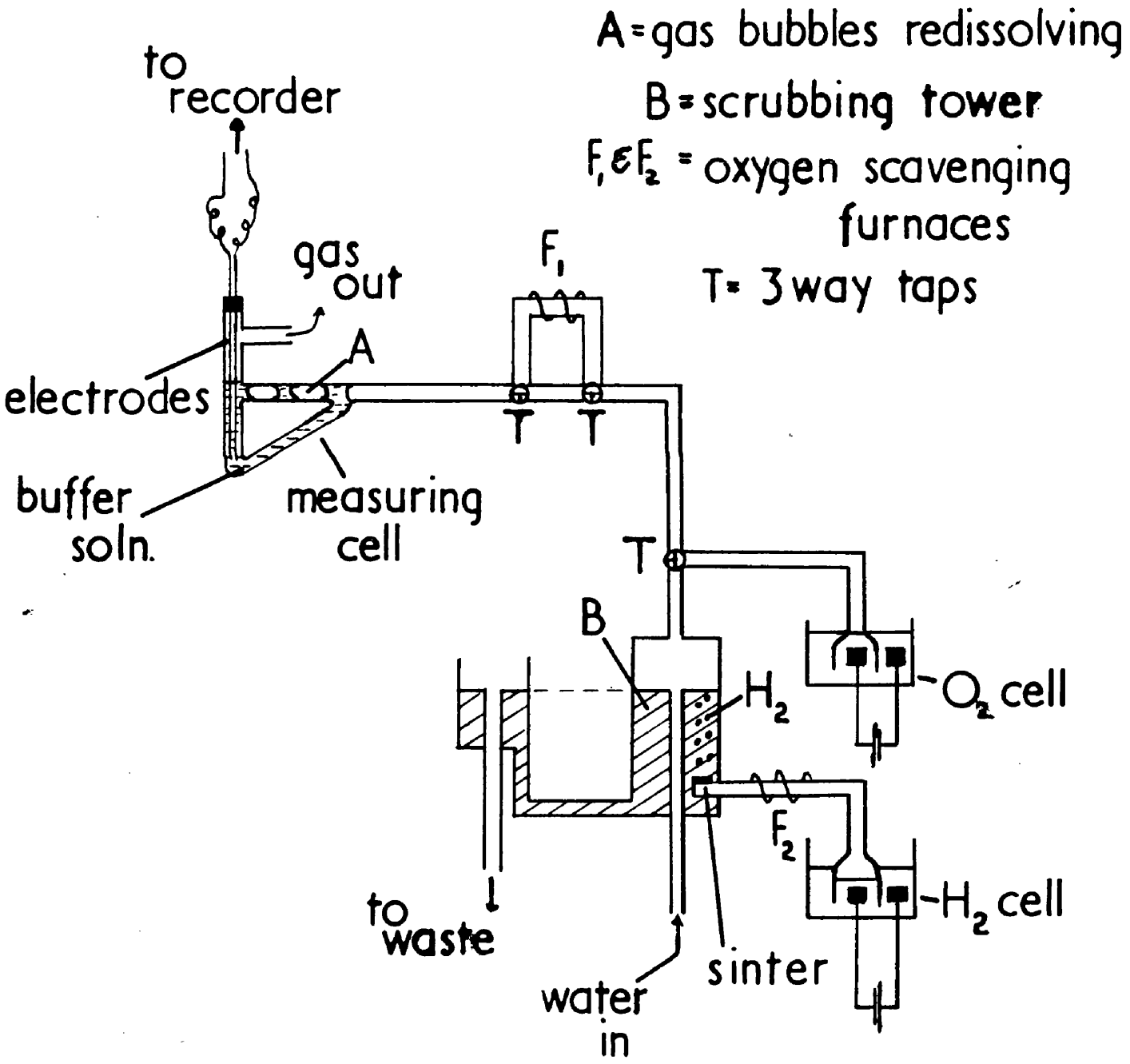


Fig. 2

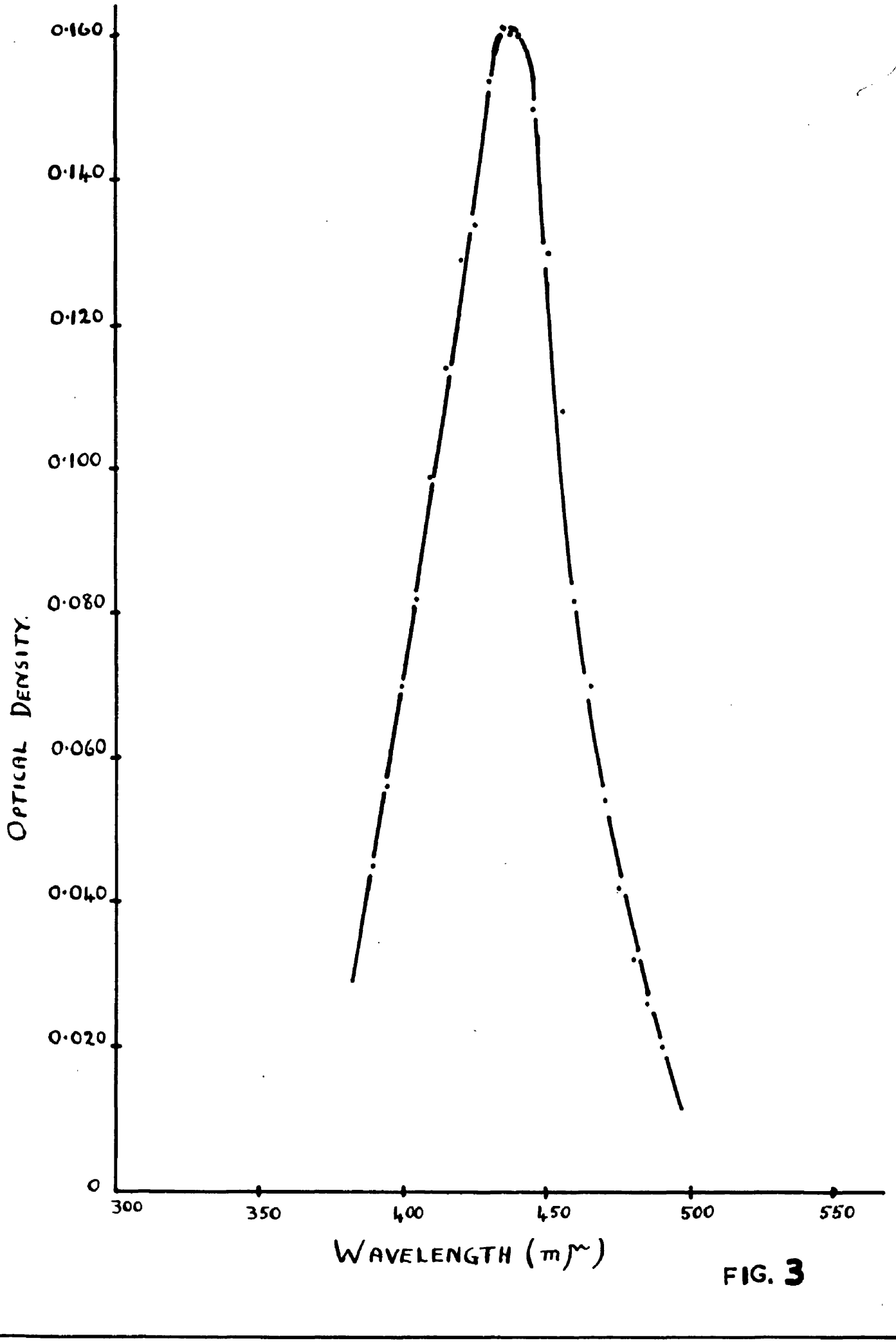

0·160
0·140
0·120
0·100
0·080
0·060
0·040
0·020
0
OPTICAL DENSITY.
300
350
400
450
500
550
WAVELENGTH (mμ)

FIG. 3

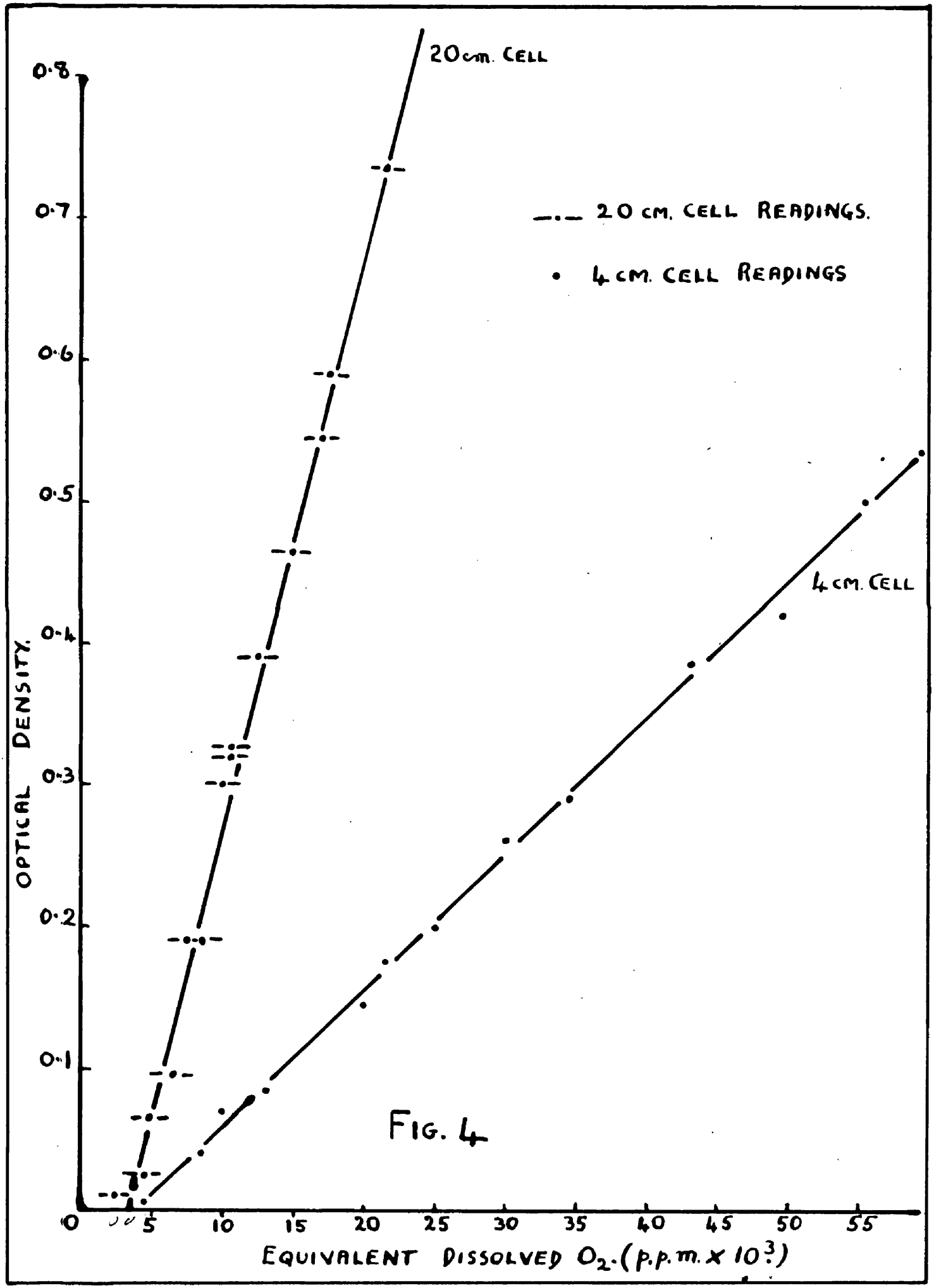
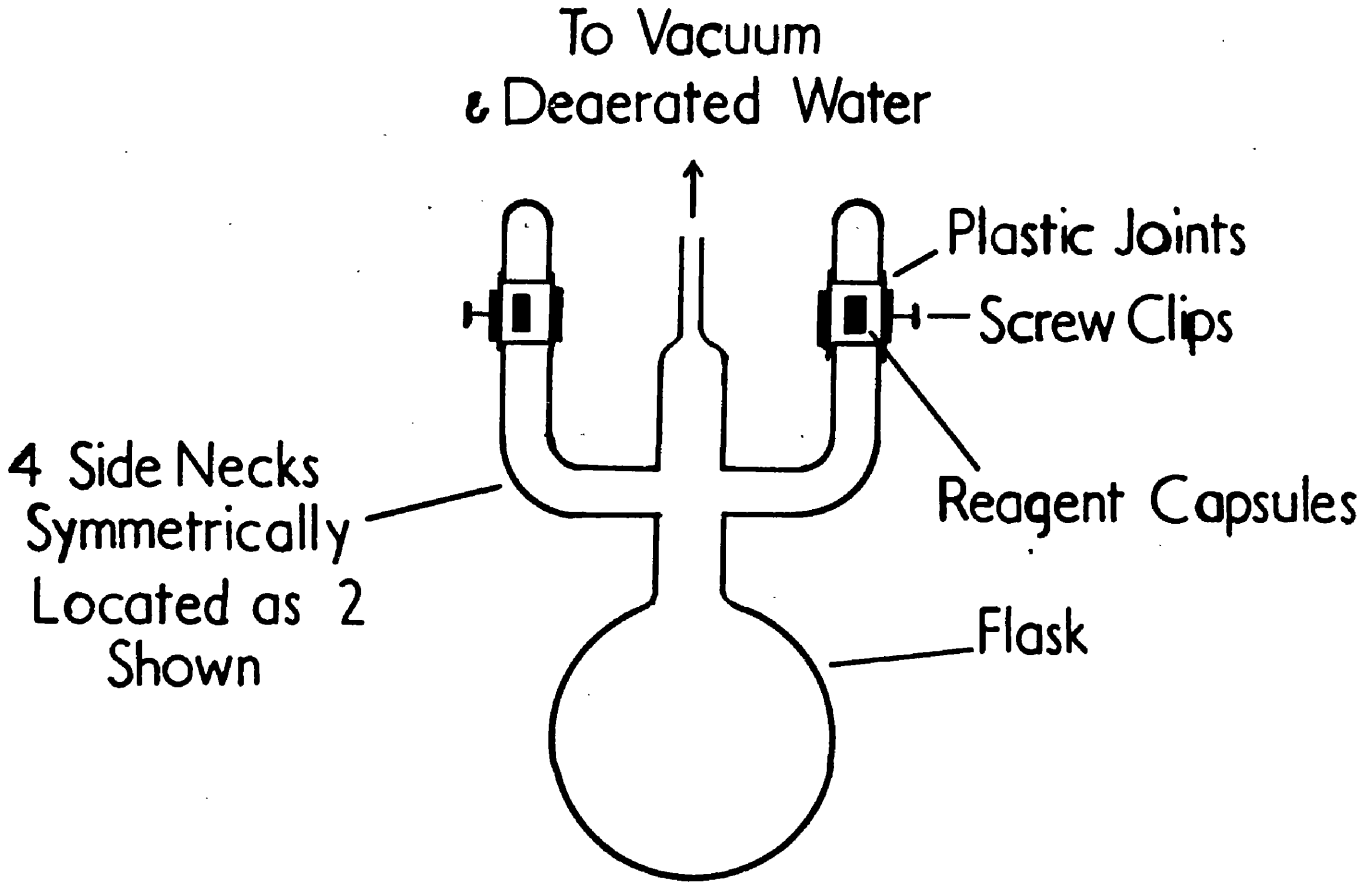

20cm. CELL
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
5
10
15
20
25
30
35
40
45
50
55
OPTICAL DENSITY.
— · — 20 cm. CELL READINGS.
• 4 cm. CELL READINGS
4 cm. CELL
EQUIVALENT DISSOLVED O_2. (p.p.m. × 10^3)

FIG. 4


To Vacuum
& Deaerated Water
Plastic Joints
Screw Clips
4 Side Necks
Symmetrically
Located as 2
Shown
Reagent Capsules
Flask

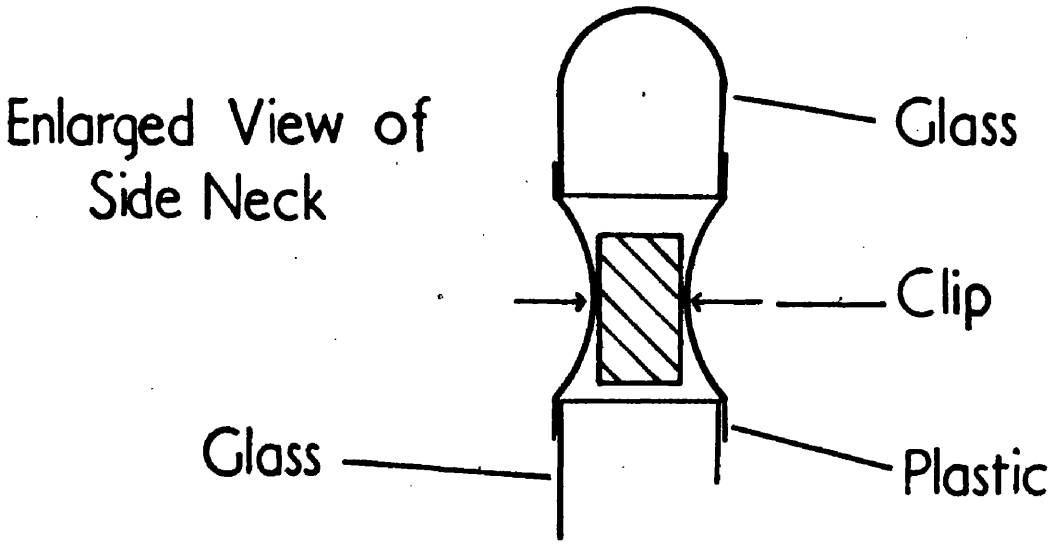

Enlarged View of
Side Neck
Glass
Clip
Glass
Plastic

Fig. 5

Preparation of "O_2-free" Reagents.

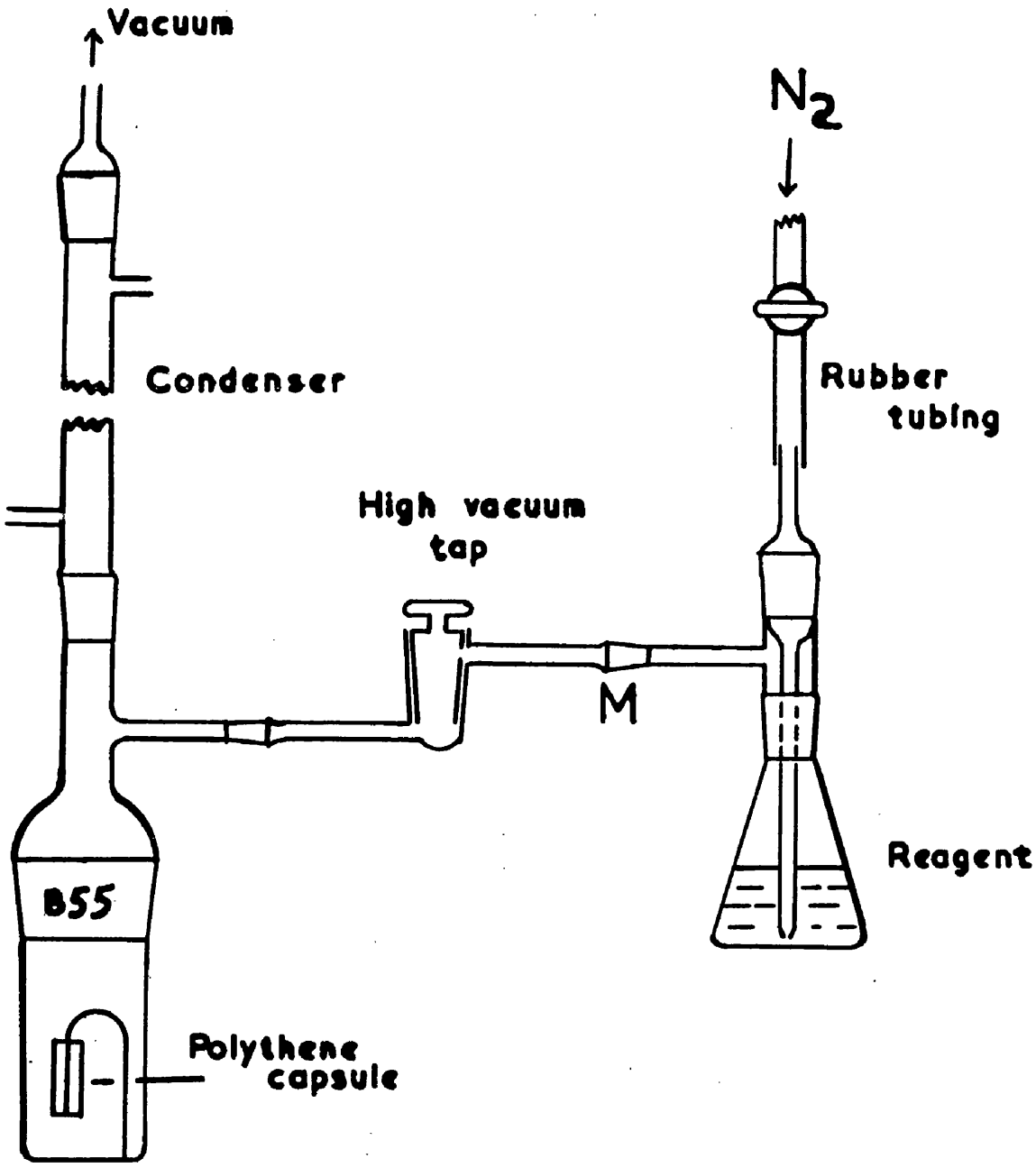


Fig. 6

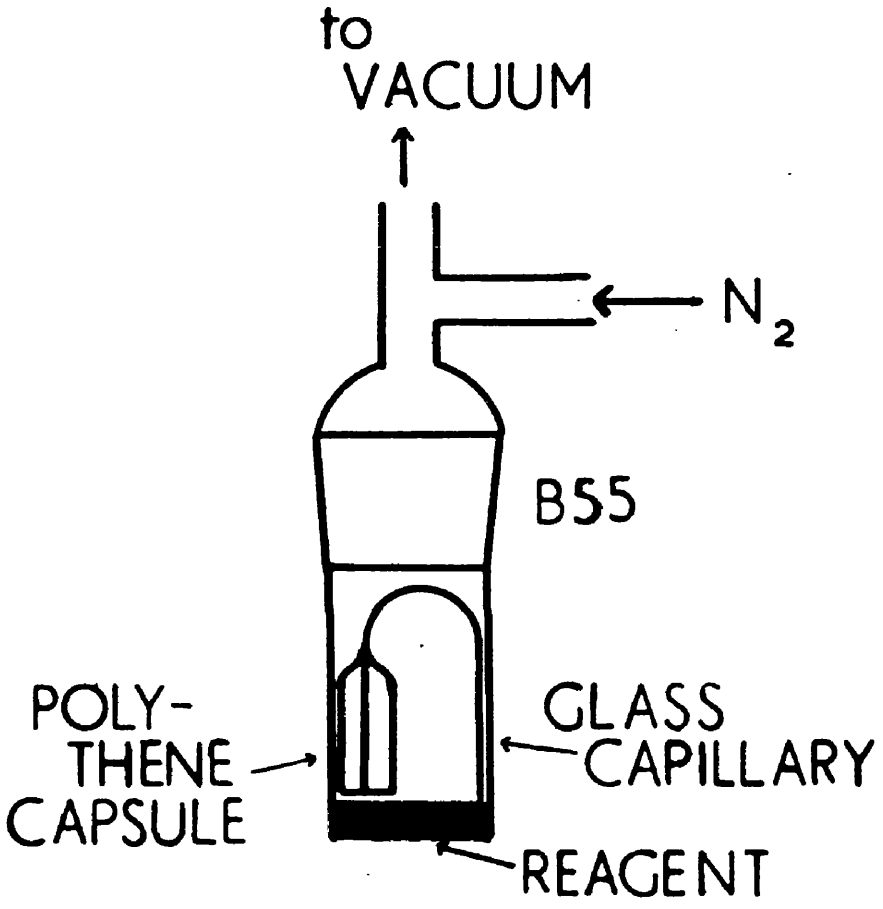

to
VACUUM
N_2
B55
POLY-
THENE
CAPSULE
GLASS
CAPILLARY
REAGENT

FIG. 7

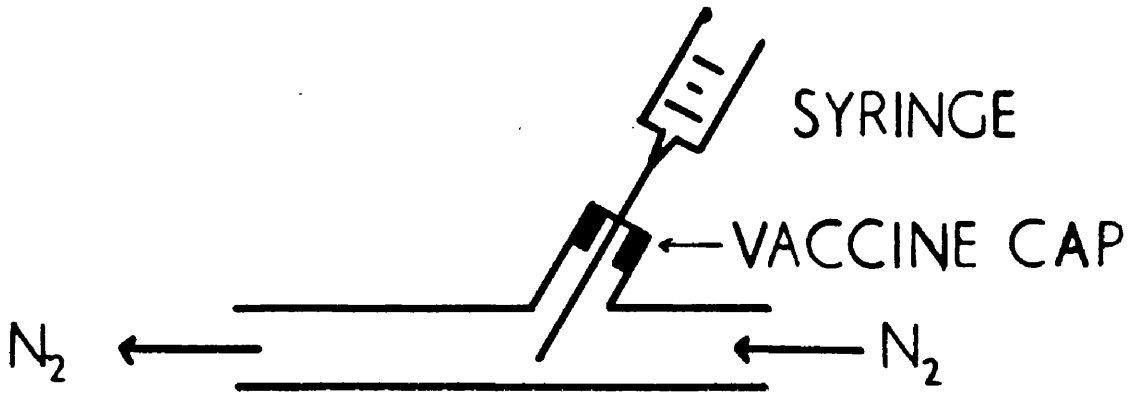

SYRINGE
VACCINE CAP
N_2
N_2

FIG. 8

Deaeration Apparatus.

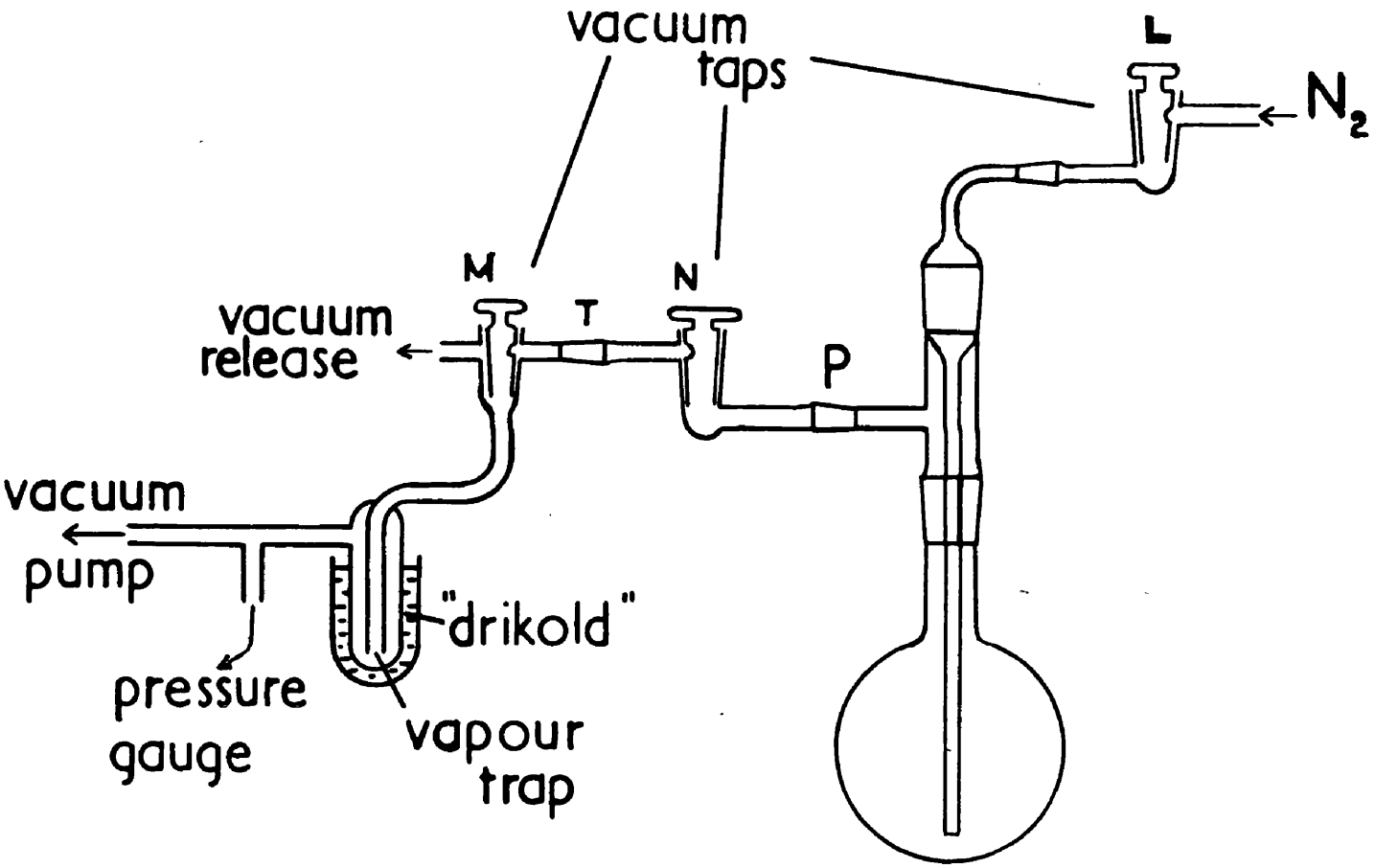


Fig. 9

OXYGEN ESTIMATION APPARATUS.

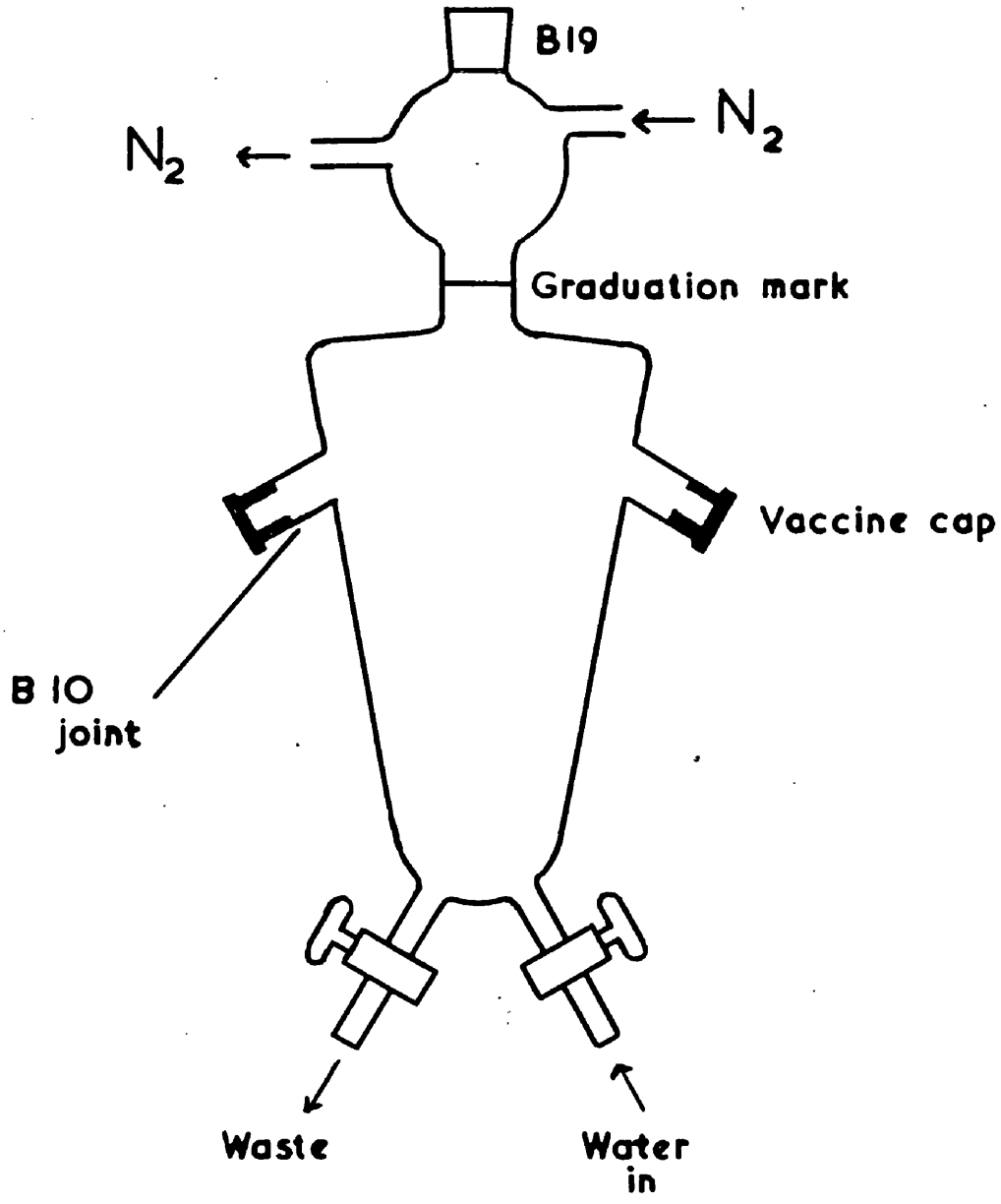


Fig. 10

Deaeration by Boiling.

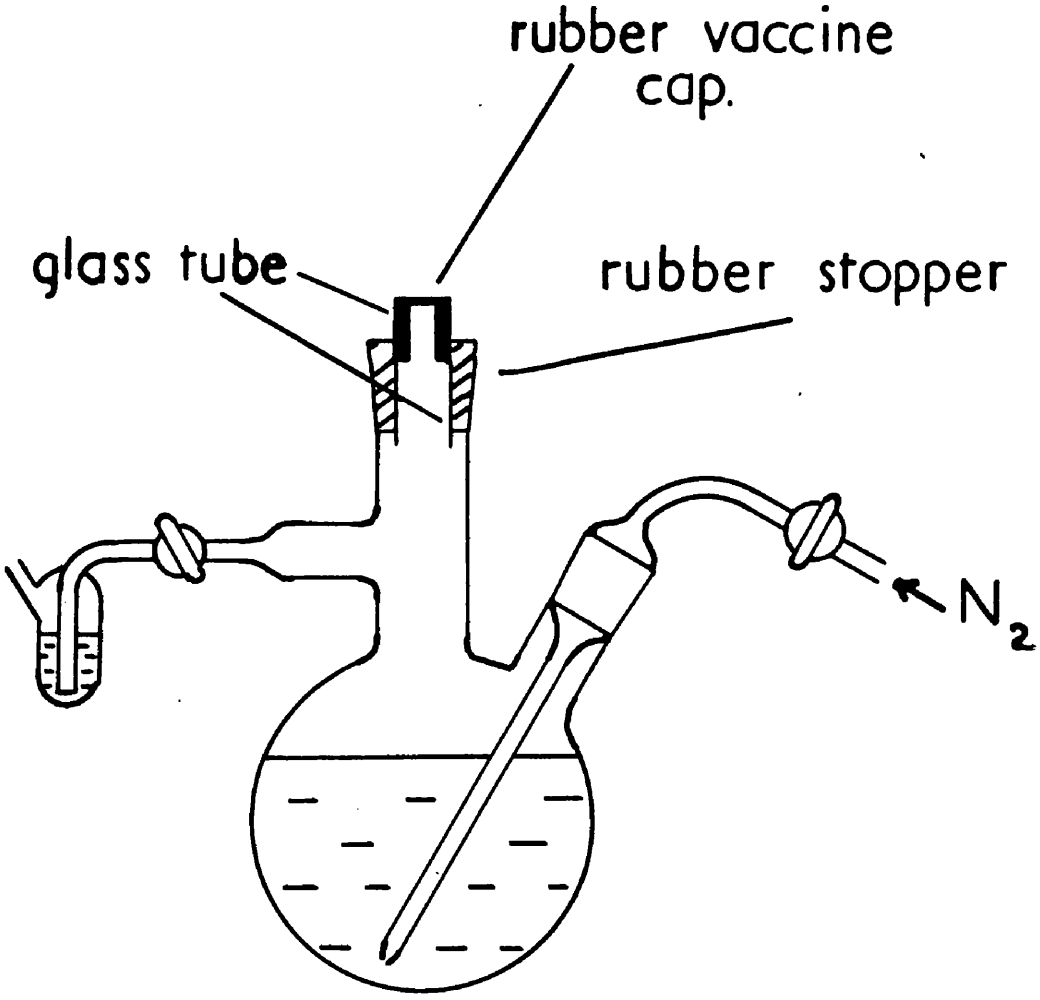
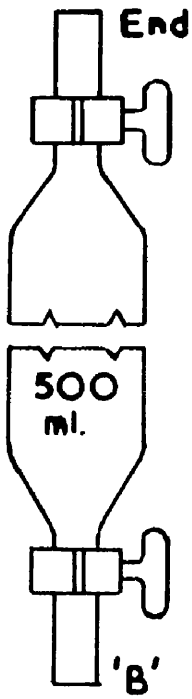


Fig. 11

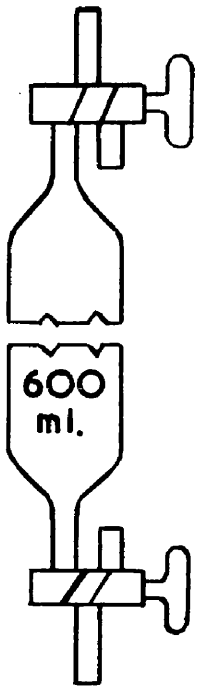
Sampling Tubes.

Mc Lean



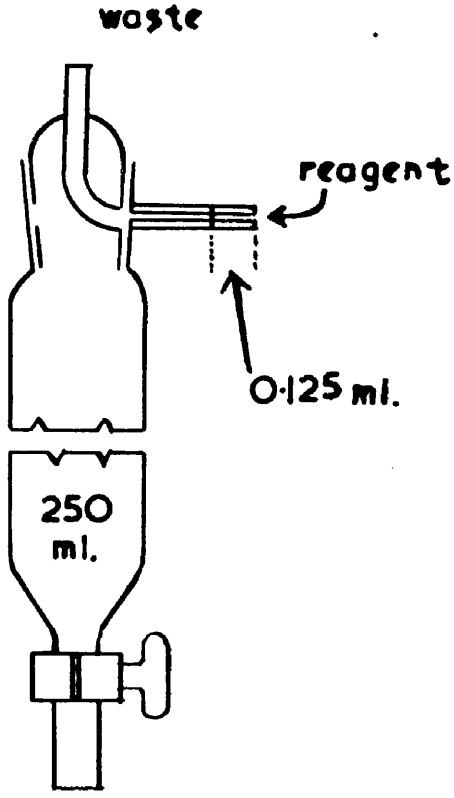
(a)

Water Pollution Board



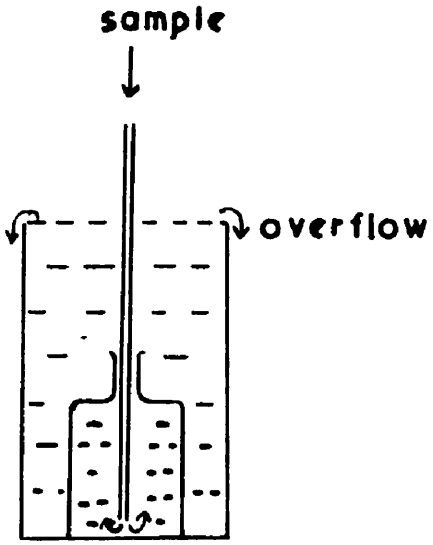
(b)

Potter



(c)

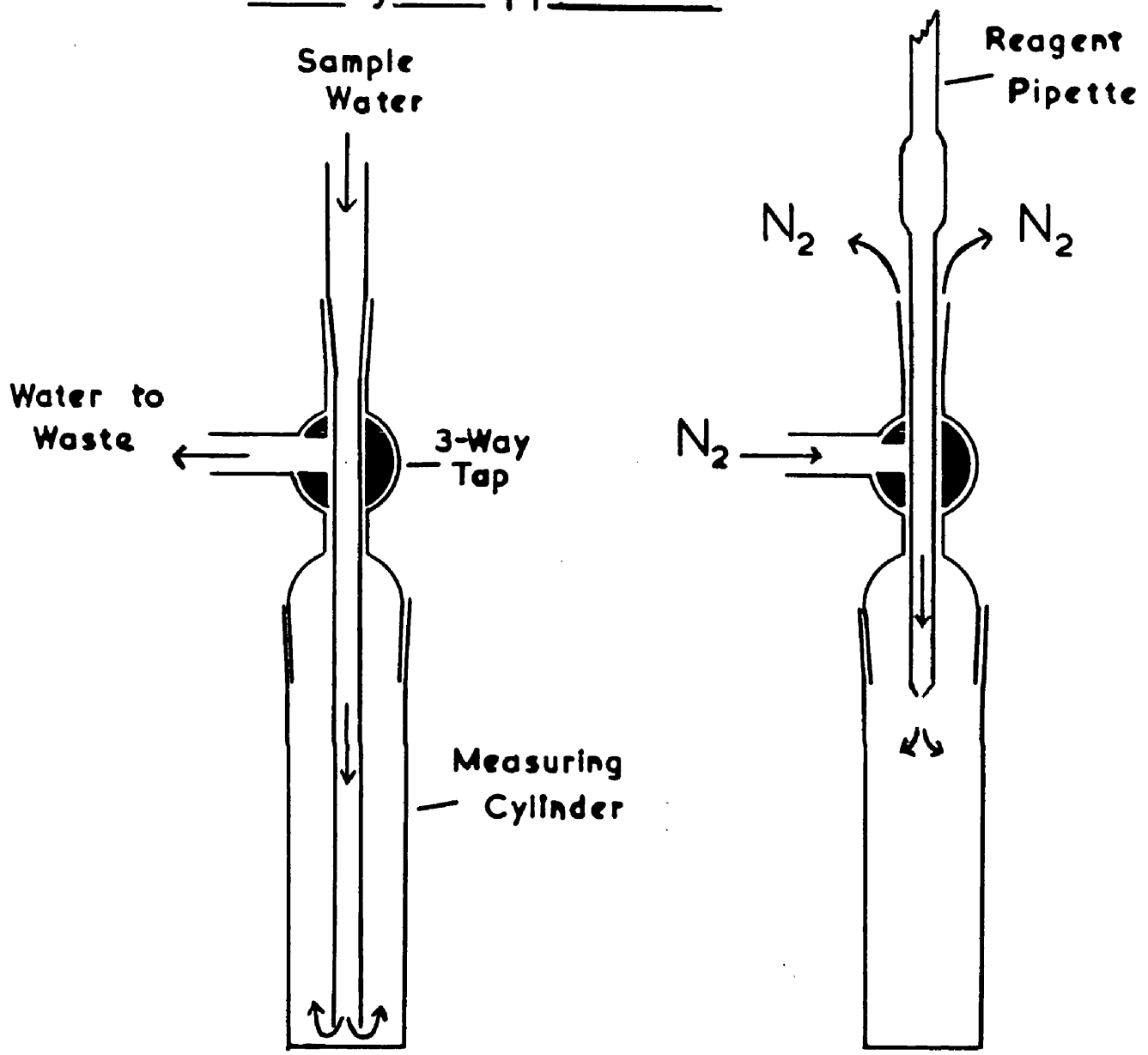
Submerged Bottle



(d)

FIG. 12

Young's Apparatus.



Deaeration of Reagents

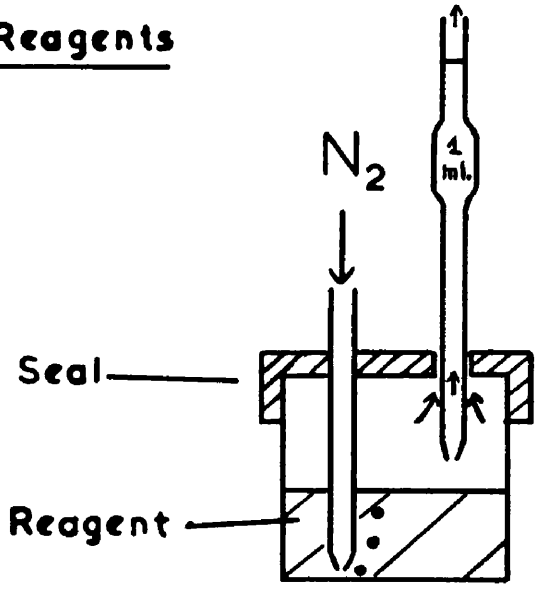


Fig. 13

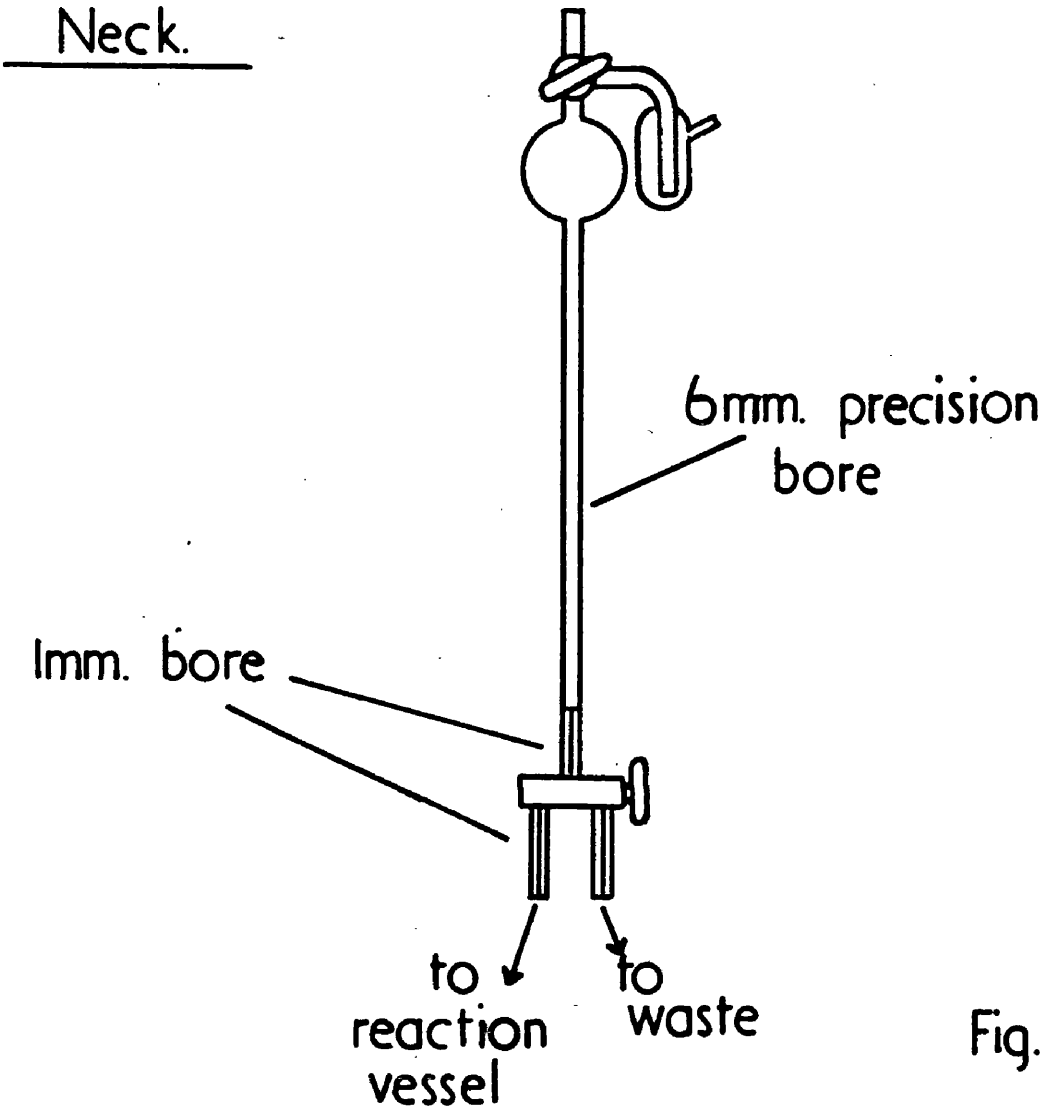


Fig. 14

Gas Washing Train.

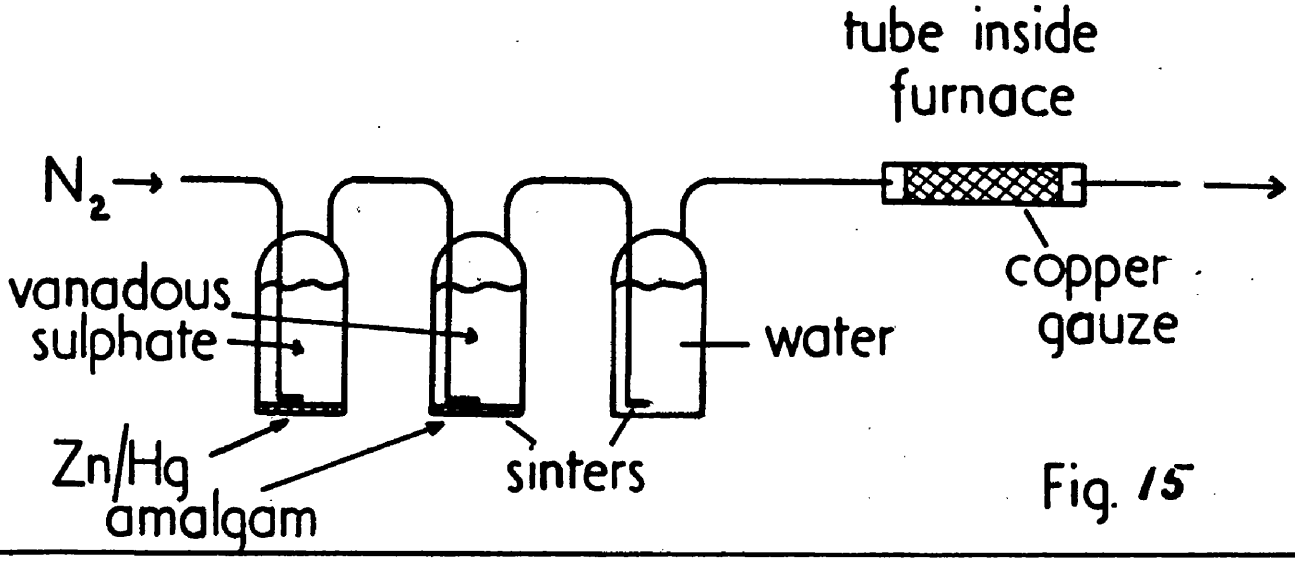


Fig. 15

Deaeration Flask.

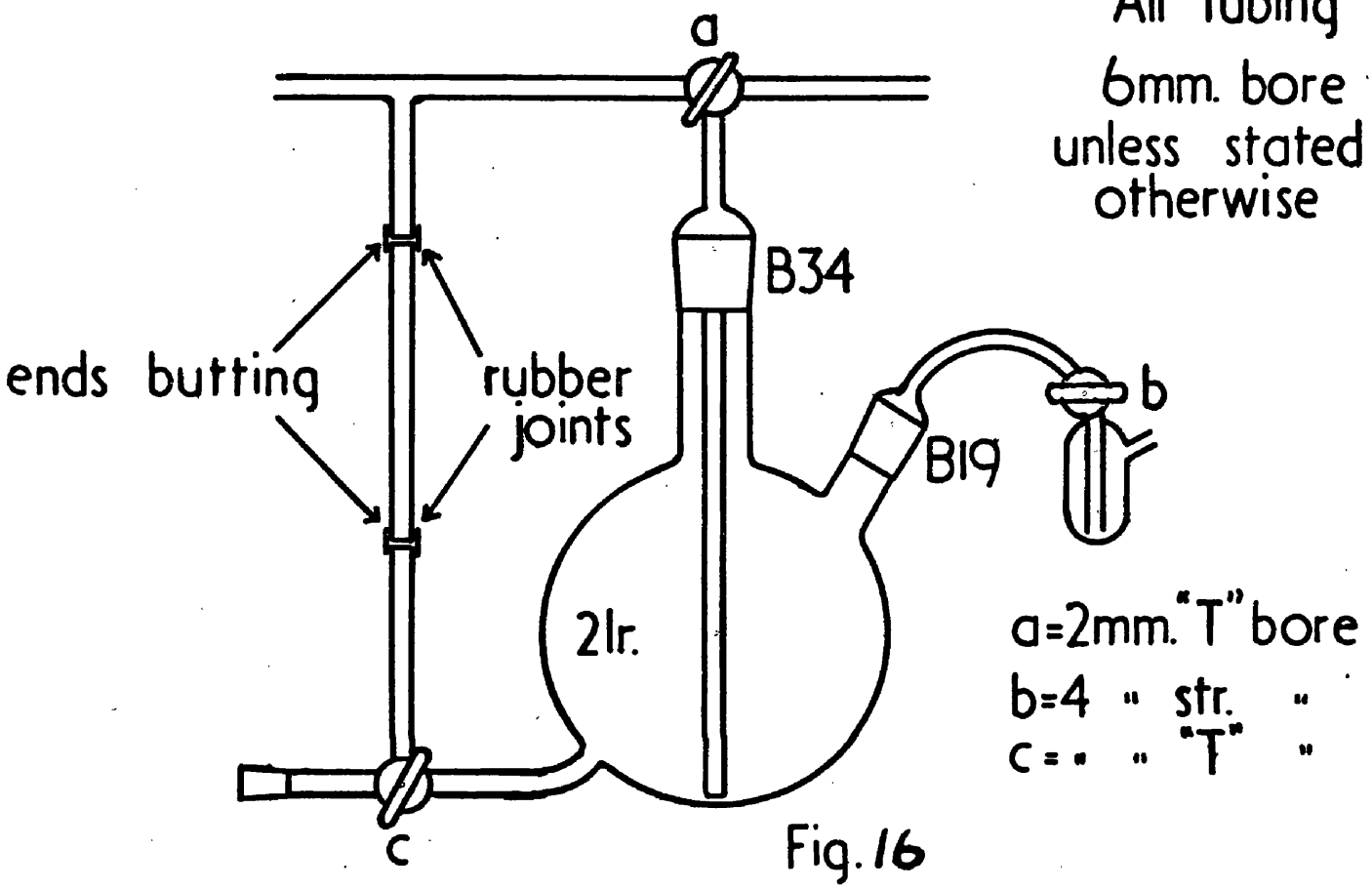


Fig. 16

Cooler (13 coils)

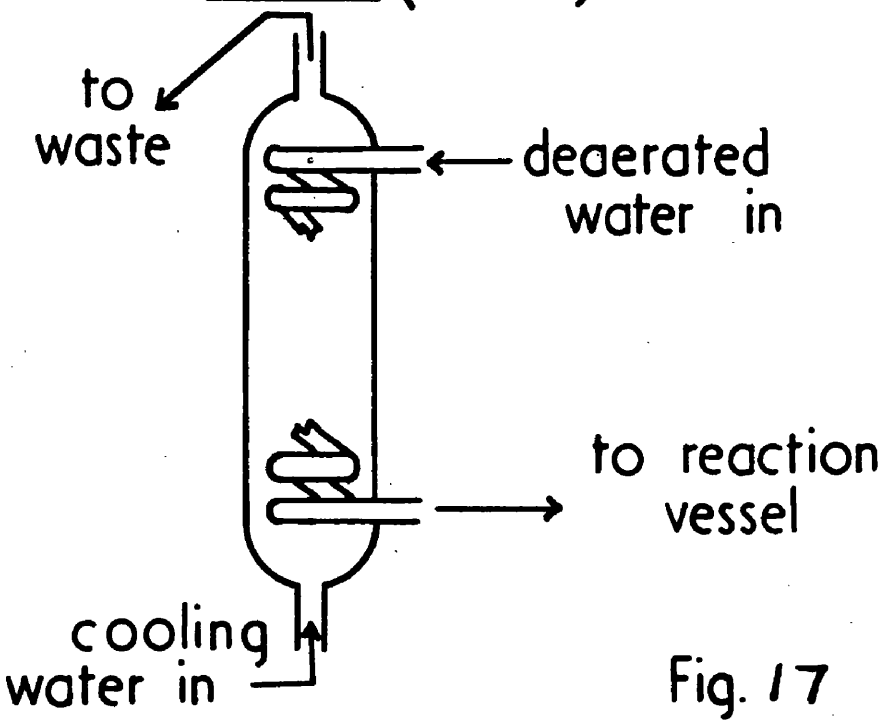


Fig. 17

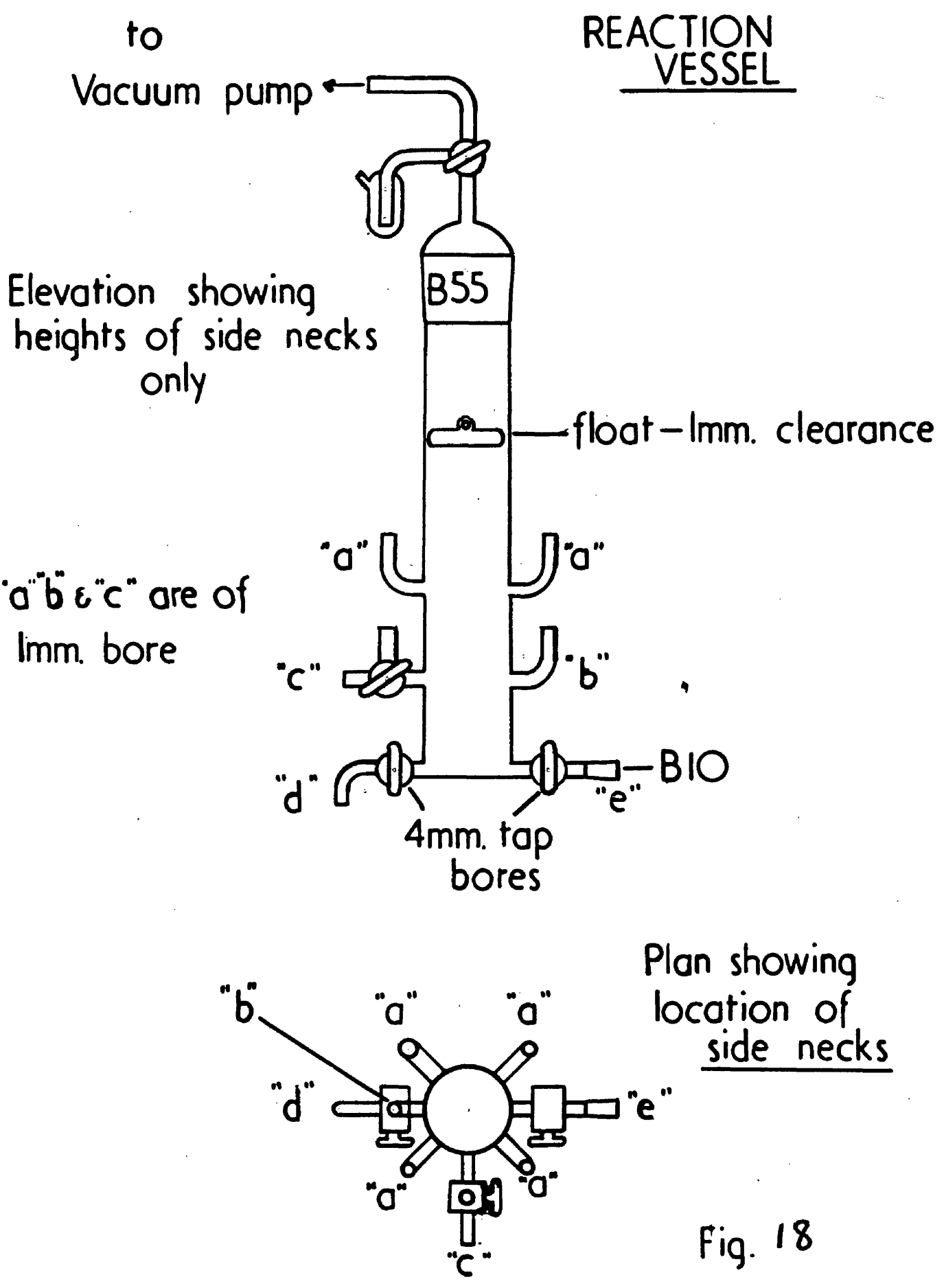
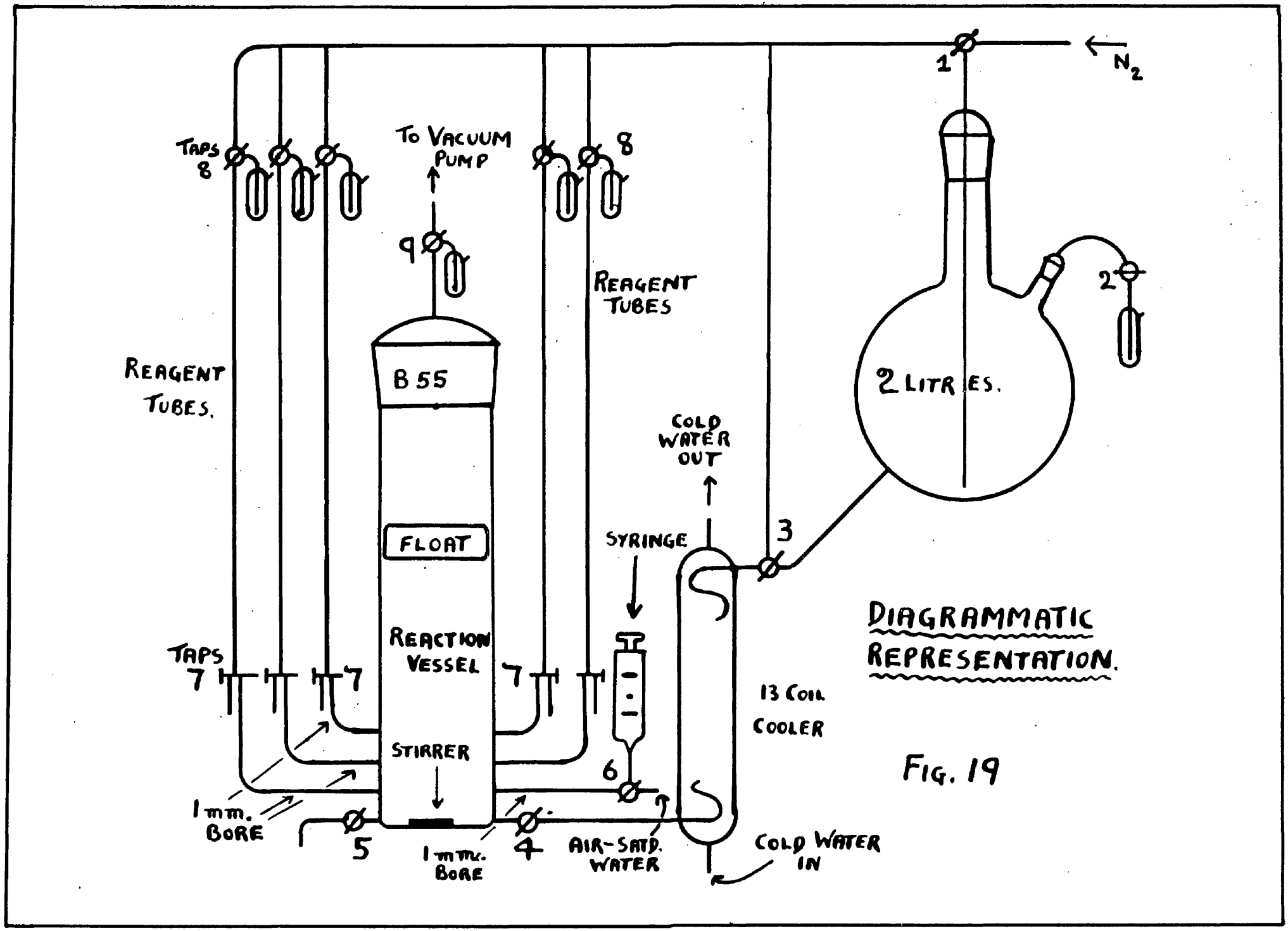

to
Vacuum pump
REACTION VESSEL
Elevation showing heights of side necks only
B55
float – 1mm. clearance
"a" "a"
"a" "b" & "c" are of 1mm. bore
"c"
"b"
"d"
"e"
B10
4mm. tap bores
Plan showing location of side necks
"b"
"a" "a"
"d"
"e"
"a" "a"
"c"

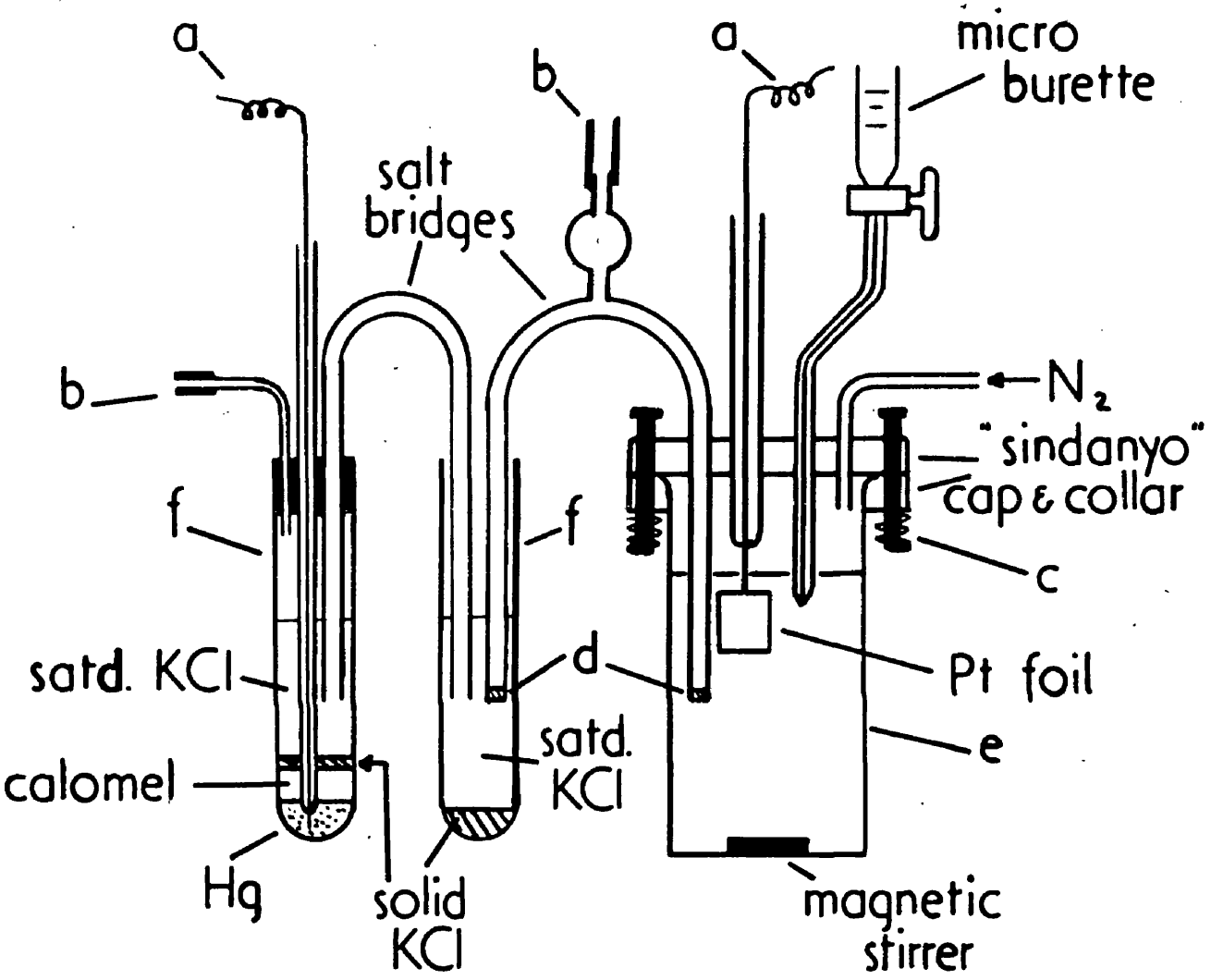
Fig. 18



DIAGRAMMATIC REPRESENTATION.

FIG. 19

TITRATION ASSEMBLY.



a = copper wire, silver soldered to platinum wire.
b = rubber tubing, closed by clips.
c = catches fitted with compression springs.
d = sintered glass.
e = spoutless beaker (600ml.)
f = "boiling" tubes.

Fig. 20

SAMPLE VESSEL.

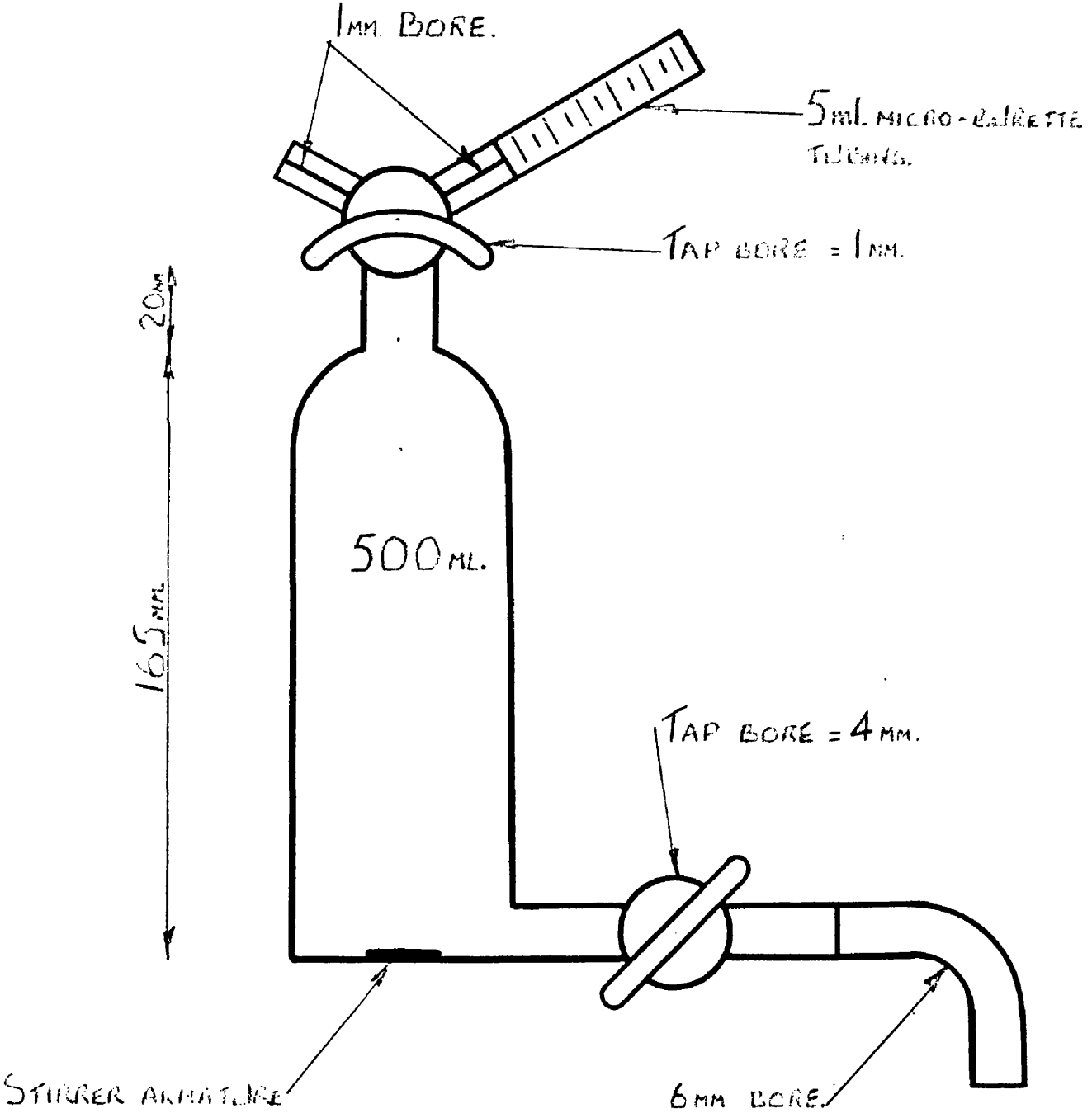


FIG. 21

FLOW CHART.

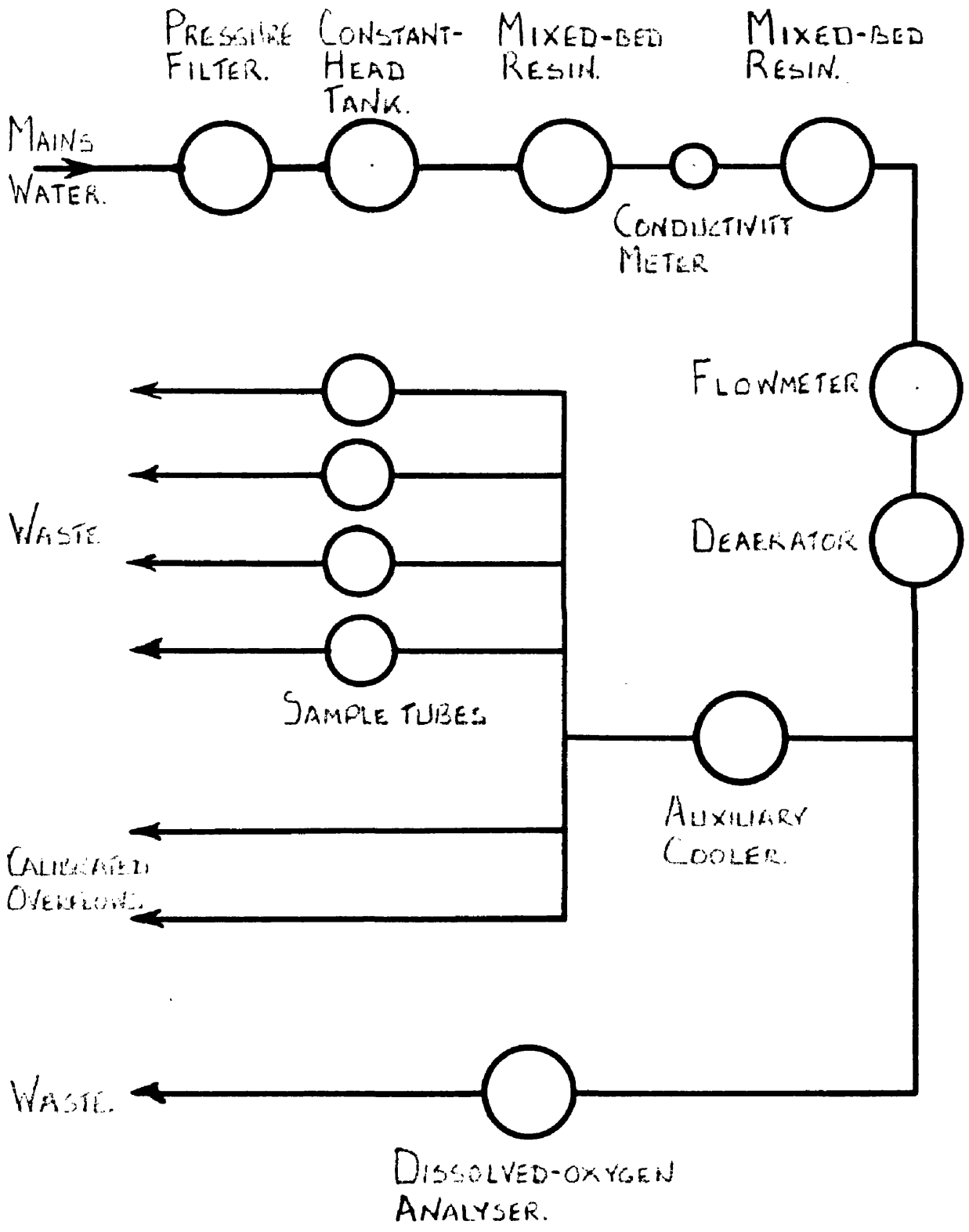
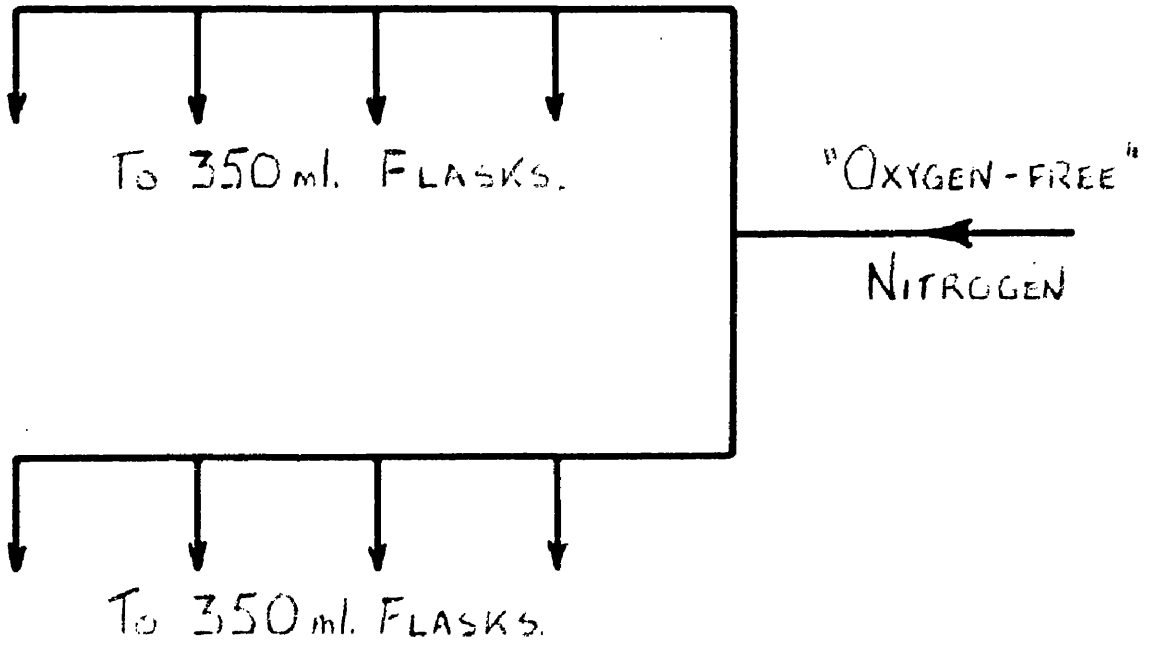


FIG. 22

"DEAERATION" of REAGENTS.



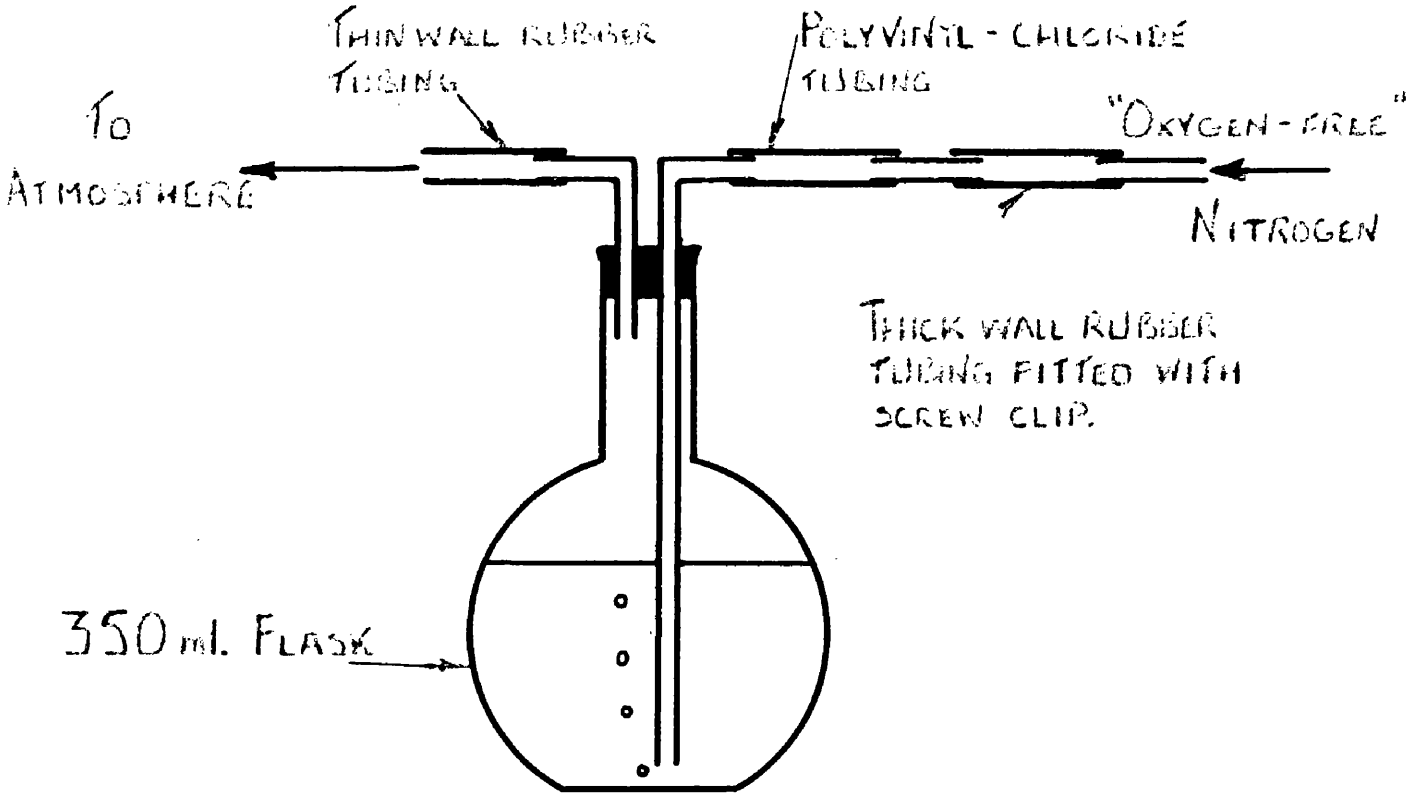


FIG. 23

ELECTRODE ASSEMBLY

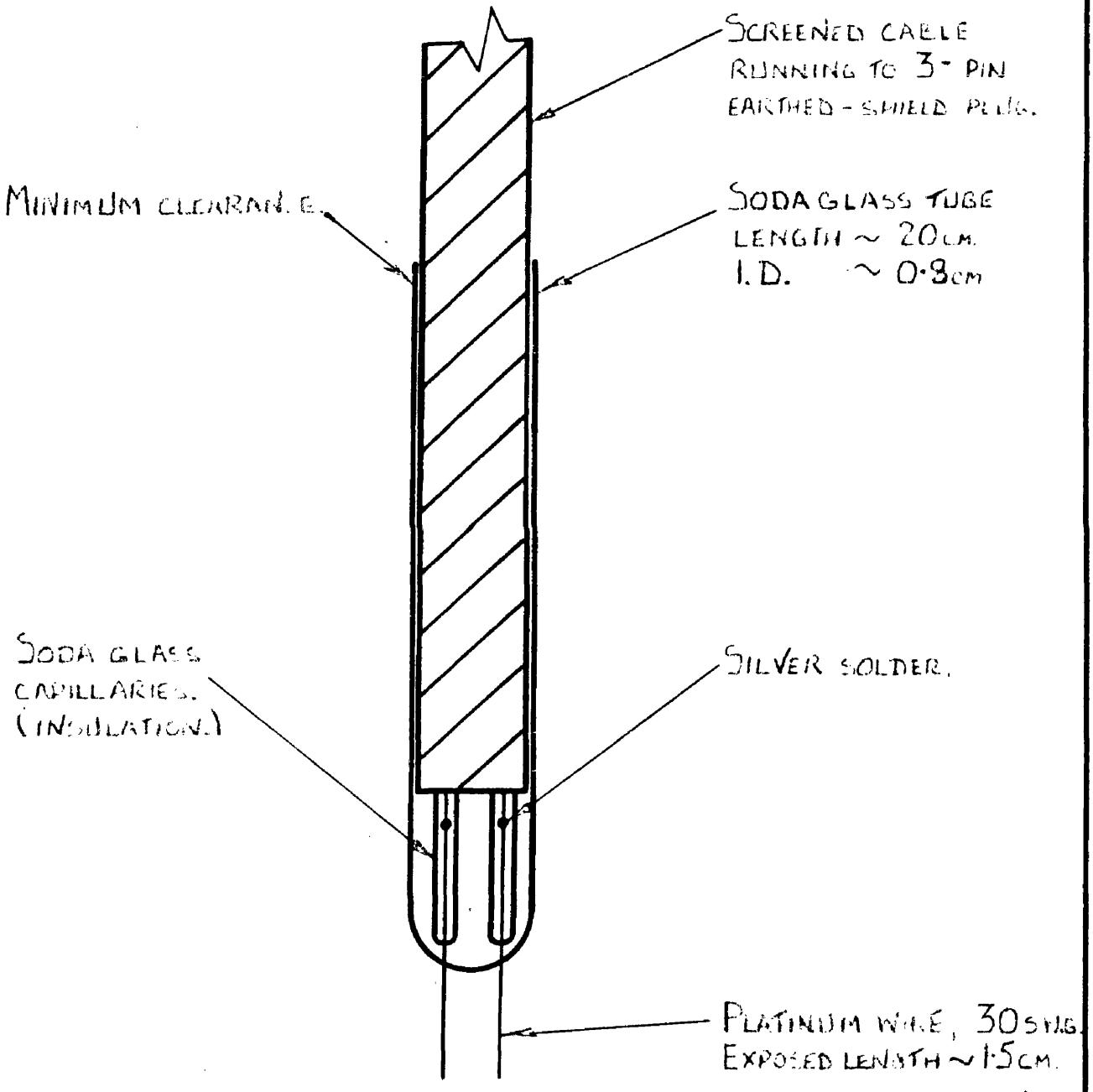
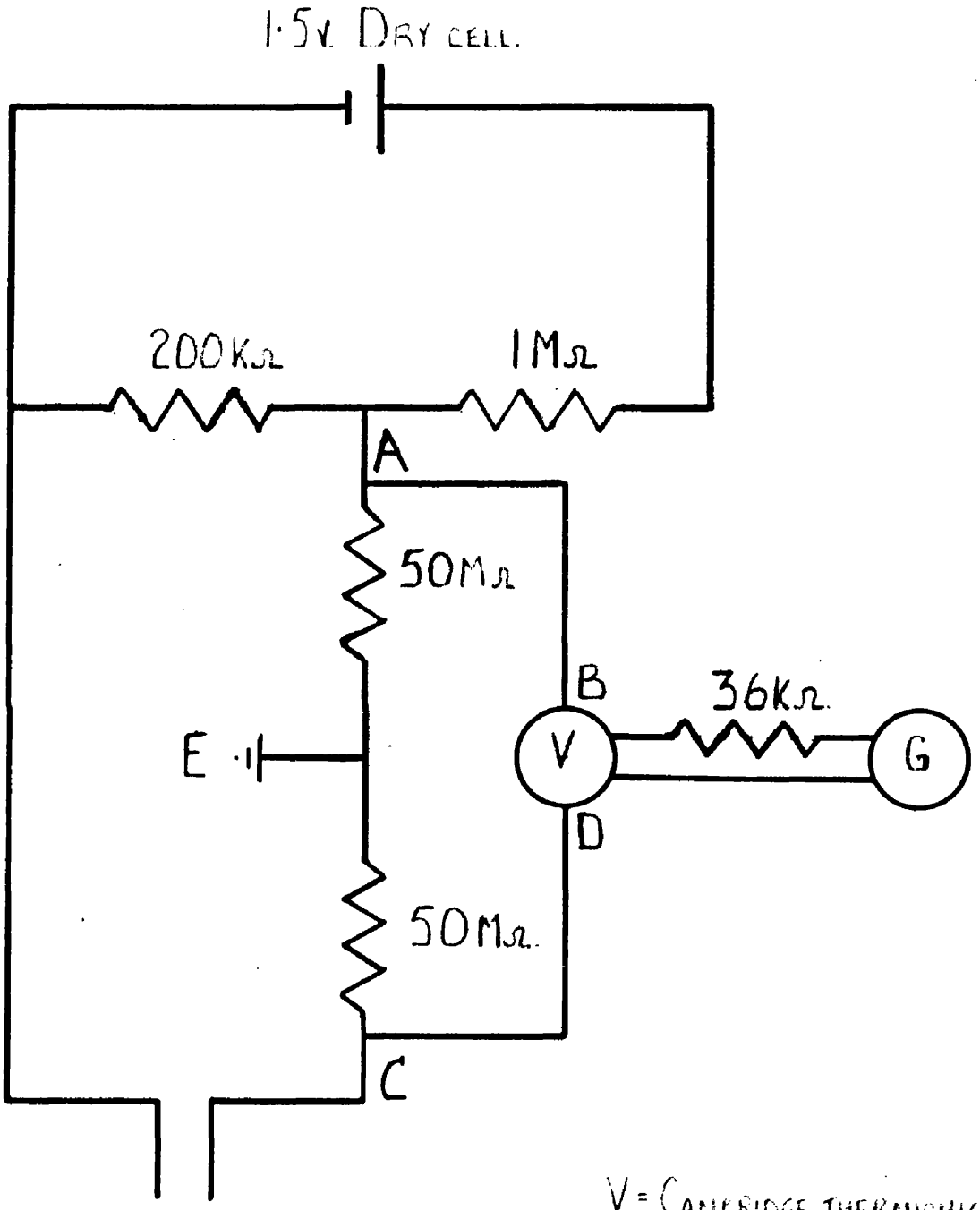


FIG. 24

PRIMARY CIRCUIT



V = CAMBRIDGE THERMIONIC POTENTIOMETER

G = CAMBRIDGE SPOT GALVANOMETER
SENSITIVITY = 170mm/μA.
100 SCALE UNITS ~ 160mm

RESISTORS ARE 0.5 WATT ± 10%
"RADIO TYPE" CARBON RESISTORS.

FIG. 25

TITRATION ASSEMBLY

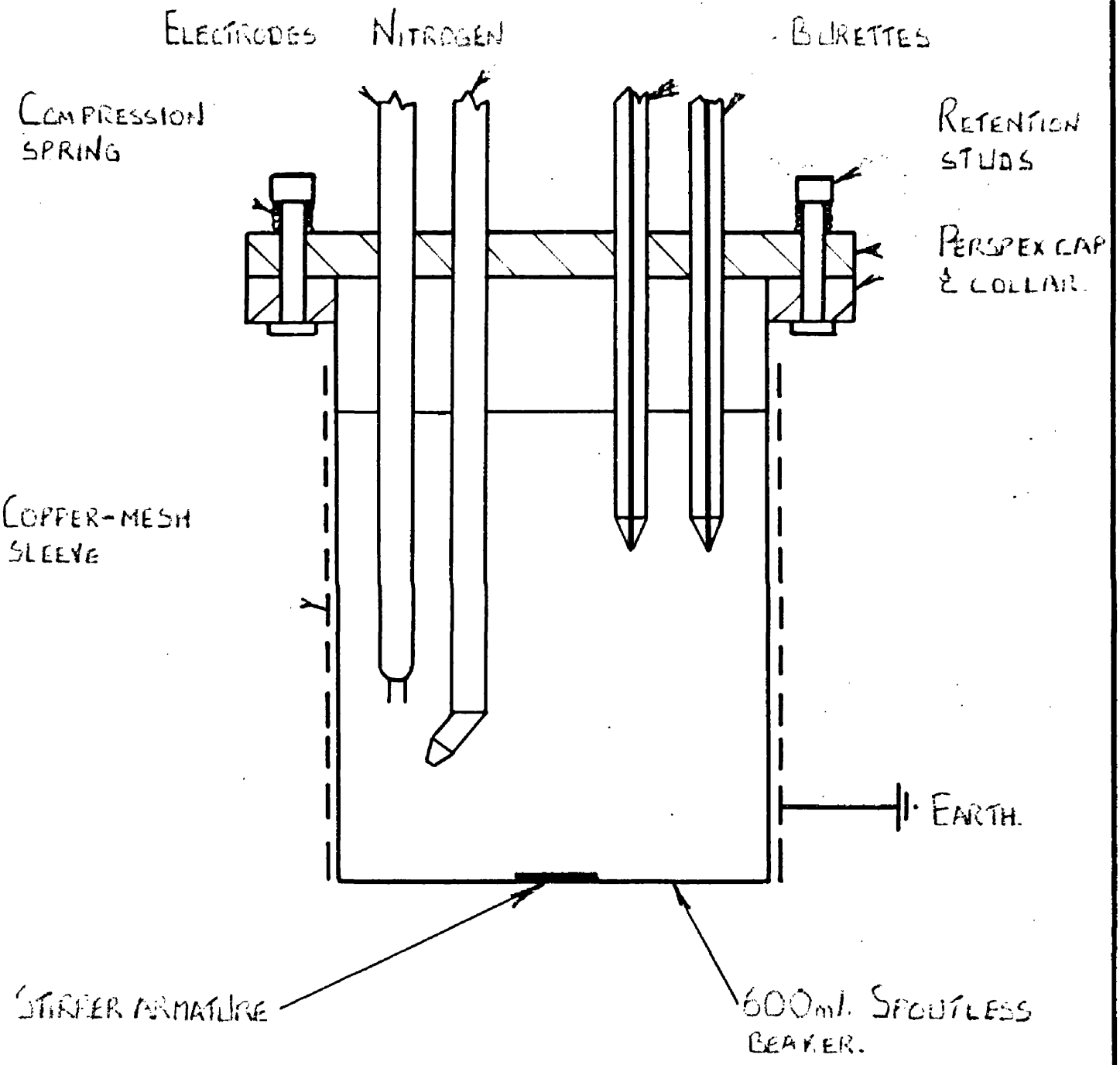


FIG. 26

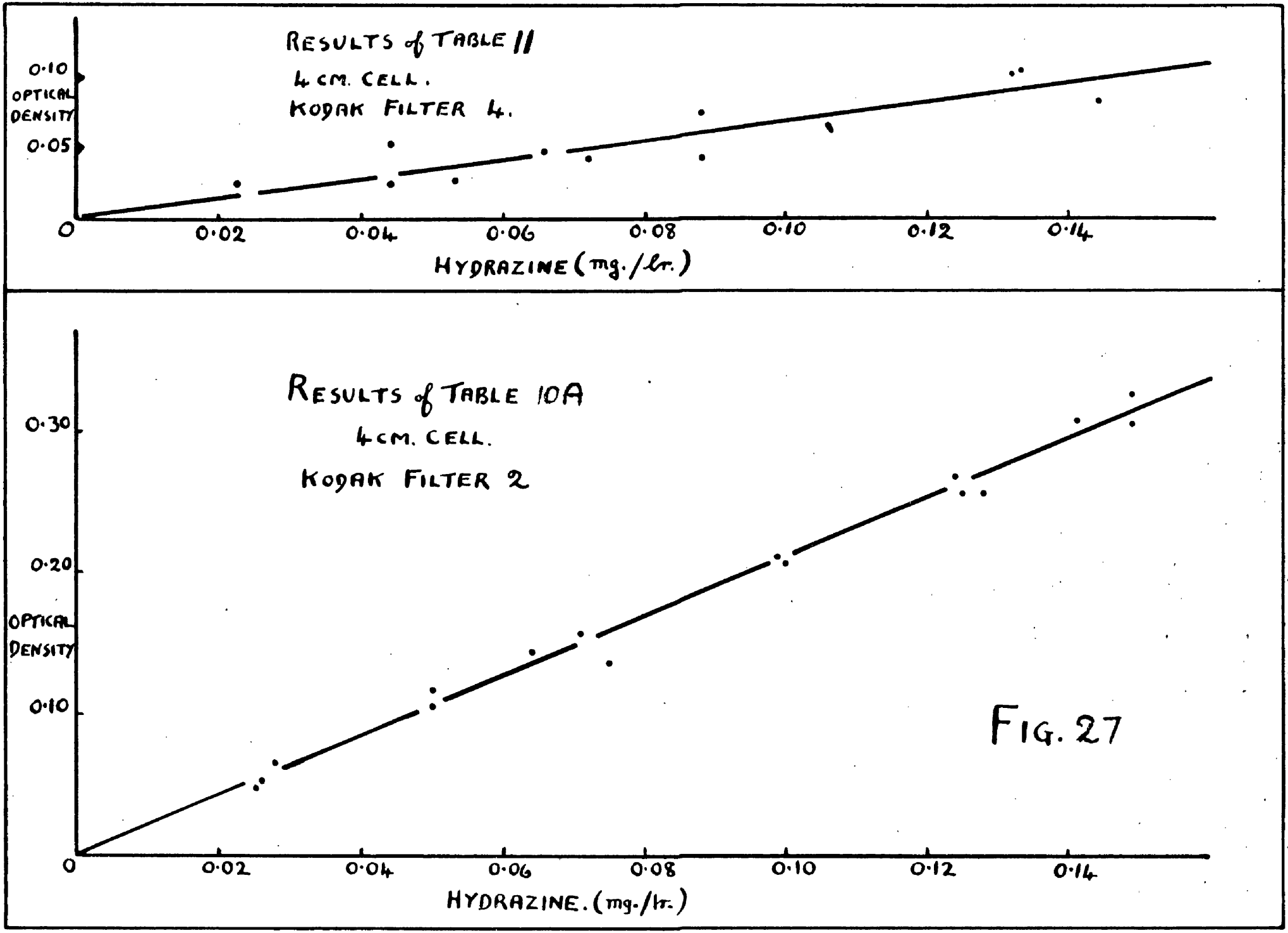

RESULTS of TABLE II
4 CM. CELL.
KODAK FILTER 4.
0·10
OPTICAL DENSITY
0·05
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
HYDRAZINE (mg./ltr.)
RESULTS of TABLE 10A
4 CM. CELL.
KODAK FILTER 2
0·30
0·20
OPTICAL DENSITY
0·10
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
HYDRAZINE. (mg./ltr.)

FIG. 27

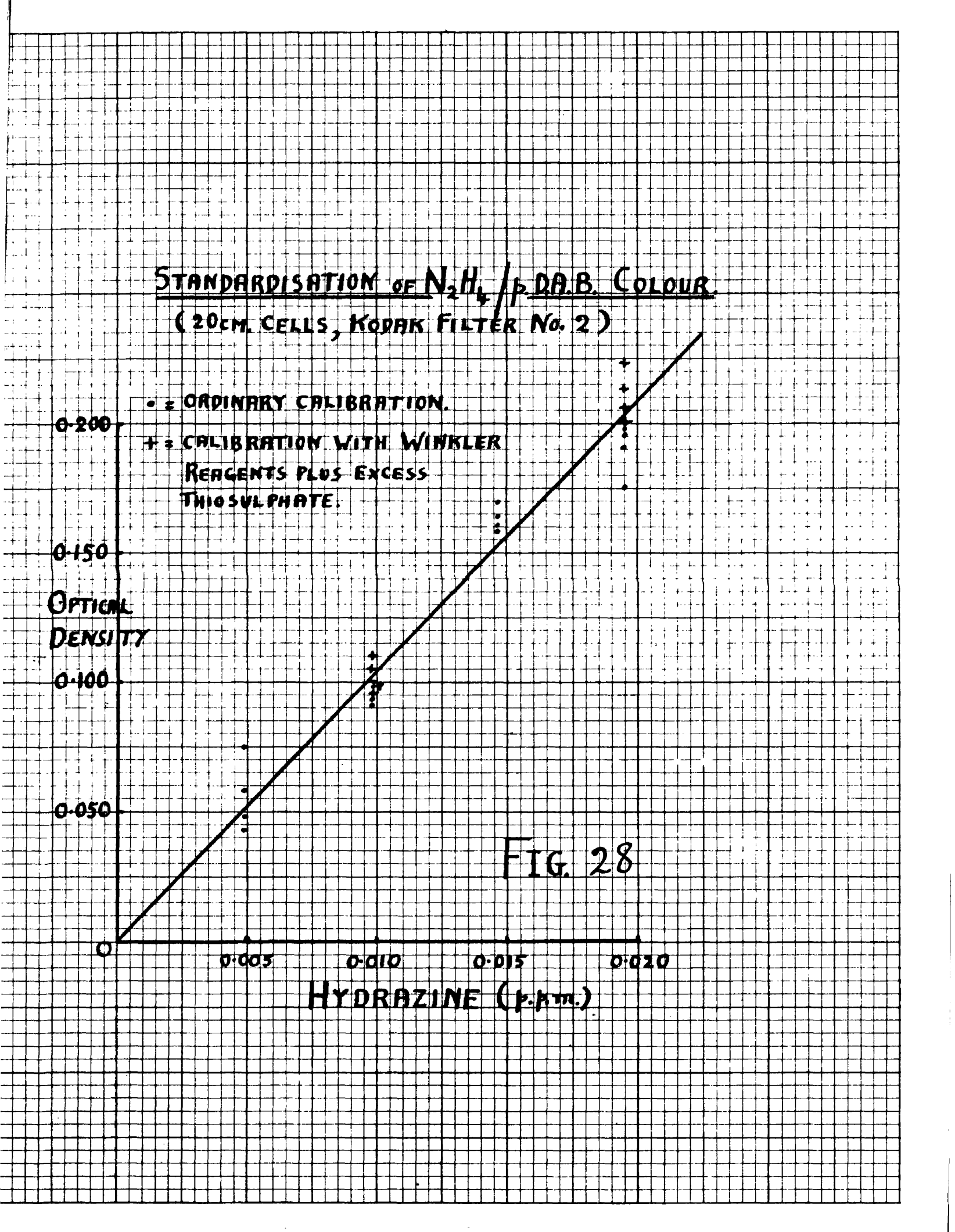

STANDARDISATION OF N_2H_4 / p-DAB. COLOUR.
(20cm. CELLS, KODAK FILTER No. 2)
• = ORDINARY CALIBRATION.
+ = CALIBRATION WITH WINKLER REAGENTS PLUS EXCESS THIOSULPHATE.
0·200
0·150
0·100
0·050
0
OPTICAL DENSITY
0·005
0·010
0·015
0·020
HYDRAZINE (p.p.m.)

FIG. 28

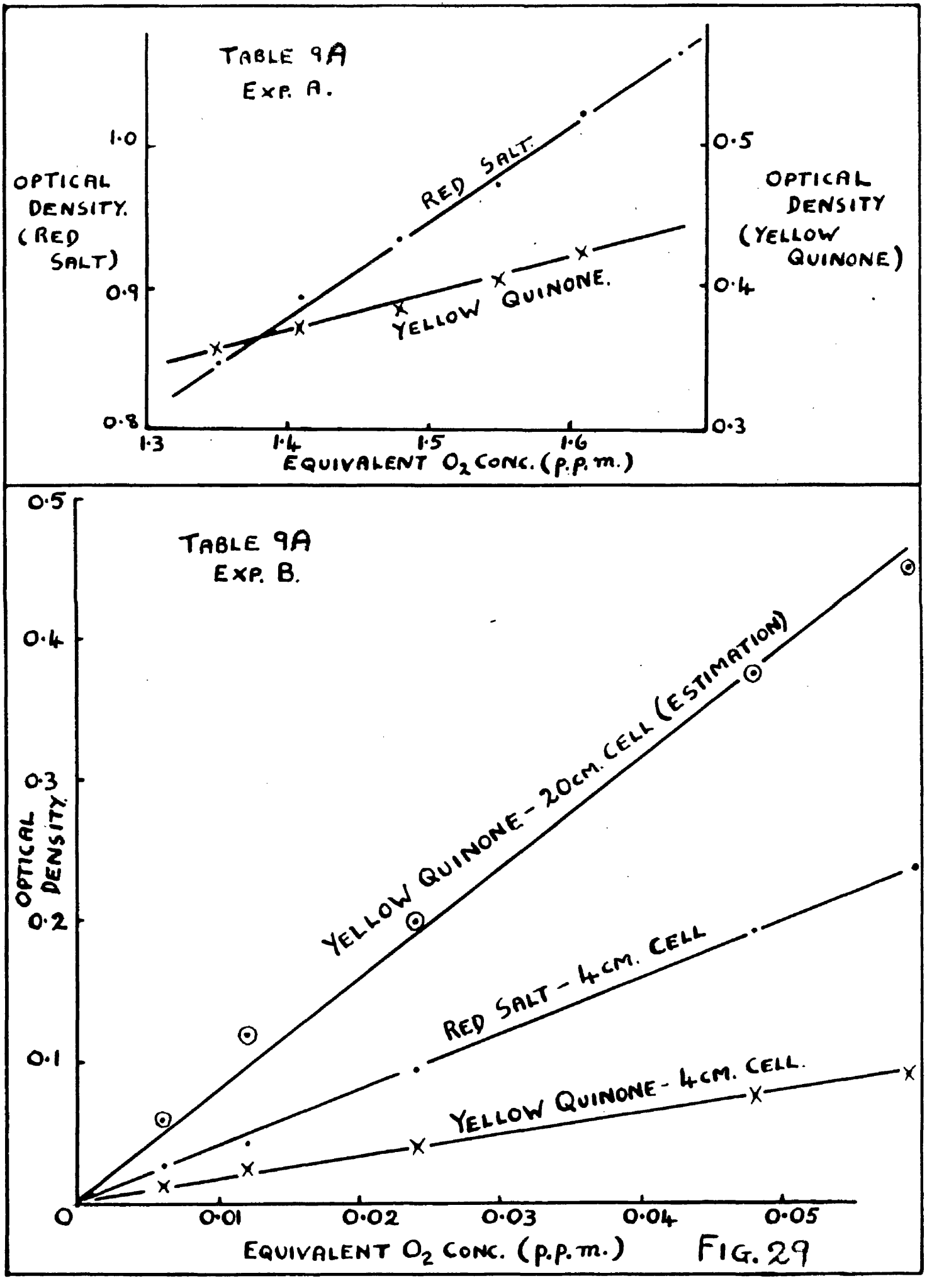


TABLE 9A
EXP. A.
1·0
0·9
0·8
OPTICAL DENSITY. (RED SALT)
0·5
0·4
0·3
OPTICAL DENSITY (YELLOW QUINONE)
RED SALT.
YELLOW QUINONE.
1·3
1·4
1·5
1·6
EQUIVALENT O_2 CONC. (p.p.m.)
TABLE 9A
EXP. B.
0·5
0·4
0·3
0·2
0·1
OPTICAL DENSITY
YELLOW QUINONE - 20cm. CELL (ESTIMATION)
RED SALT - 4cm. CELL
YELLOW QUINONE - 4cm. CELL.
O
0·01
0·02
0·03
0·04
0·05
EQUIVALENT O_2 CONC. (p.p.m.)

FIG. 29